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OF THE SECOND ANNUAL
TECHNICAL SEMINAR ON
CHEMICAL SPILLS**

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**FEBRUARY 5-7, 1985
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THE DEVELOPMENT OF A CHEMICAL SPILL EMISSION RATE MODEL

I.A. Buist, P. Eng. and R.C. Belore, P. Eng.
S.L. Ross Environmental Research Limited
Ottawa, Ontario

INTRODUCTION

A simple, yet accurate technique is needed to predict the rate at which chemicals (liquid or gaseous) leak from damaged storage or transportation containers. Accurate predictions of the outflow rate and duration of the incident are vital for the planning of a safe and effective emergency response. Of particular importance to the response effort is the "source strength" component of the release. This source term is required by all atmospheric dispersion models which predict the areas which should be evacuated due to the release of the hazardous chemical.

Nomograms for predicting these chemical leak rates and durations were developed for the EnviroTIPS series of manuals (Environment Canada, 1983). Unfortunately many simplifications were made in the development of these nomograms in order to make them easy to use. For example, a number of assumptions were made to force the prediction of a maximum rate of release. This may or may not represent a "worst-case situation" for some accidents. A slow emission rate for a very toxic substance may necessitate the evacuation of a large area for the entire leak period. A model which is forced to generate maximum release rates would falsely predict a much shorter hazard period.

The objective of this study is to improve upon the existing nomograms by using more rigorous mathematical expressions for the transfer processes involved (heat, fluid and mass). The resulting system of equations will be modelled numerically on a micro-computer. This permits the rapid solution of the iterative balance equations and thus reduces the number of simplifying (and often misleading) assumptions needed to predict the release characteristics. Sensitivity analyses using the detailed computer model will establish which, if any, parameters and assumptions can be omitted from the final model without detracting from its accuracy.

The end result of this study will be a new series of more detailed nomograms derived from the computer model which can be used with only a few simplifications or assumptions to predict chemical leak rates and durations for a wide range of conditions.

THE PROBLEM

In order to be as accurate as possible the model will include expressions to cover at least the following factors:

Accident Factors

puncture - position (above, at or below liquid level)
 - size (down to pin hole size)
 - shape

ambient temperature

amount of insulation destroyed

formation of ice - on the liquid surface
 - in the puncture

Tank Factors

head height

type (square, rectangular, cylindrical, spherical)

orientation (vertical, horizontal)

size

insulation

location - above ground
 - on ground
 - in water

wall thickness/material

Substance Factors

phase

boiling point

evaporation rate

evaporative cooling

vapour pressure

viscosity

diffusion rate/molecular size

The model will be applied, initially, to the following chemicals:

- * chlorine
- * benzene
- * hydrogen sulphide
- * anhydrous ammonia
- * sulphuric acid (66°Be)

THE MODEL

The following is an example of the equations used to predict the outflow rate from a rupture in a cylindrical storage tank containing a volatile liquid.

From the Bernoulli equation it can be shown that:

$$\text{Eqn. 1} \quad \dot{M} = C_D Y A_R \left(\frac{2(P_1 - P_2) \rho_1}{1 - \beta^4} \right)^{1/2}$$

where: $\dot{M}$ = mass outflow rate (Kg/s)
 C_D = discharge coefficient (determined experimentally)
 Y = expansion factor
 A_R = area of rupture (m^2)
 P_1, P_2 = internal and external pressures at rupture (N/m^2)
 ρ_1 = density of fluid at P_1 (Kg/m^3)
 β = ratio of rupture diameter to tank diameter

For an incompressible fluid:

$$\text{Eqn. 2} \quad Y = 1$$

For a compressible fluid at subsonic velocity:

$$\text{Eqn. 3} \quad Y = 1 - \left(\frac{1-r}{K} \right) (0.41 + 0.35\beta^4)$$

where: $r = P_2/P_1$
 K = ratio of specific heat (C_p/C_v)

For a compressible fluid at sonic velocity,

$$\text{Eqn. 4} \quad r^{(1-K)/K} + \left(\frac{K-1}{2} \right) \beta^4 r^{2/K} = \frac{K+1}{2}$$

$$\text{Eqn. 5} \quad \dot{M} = C_D A_R \left(K \left(\frac{P_1}{V_1} \right) \left(\frac{2}{K+1} \right)^{(K+1)/(K-1)} \right)^{1/2}$$

where: v_1 = specific volume of gas at P_1 (m^3/Kg)

Figure 1 shows two possible orientations for tanks and defines certain variables. For this example Case B is selected, with the rupture below the incompressible liquid level.

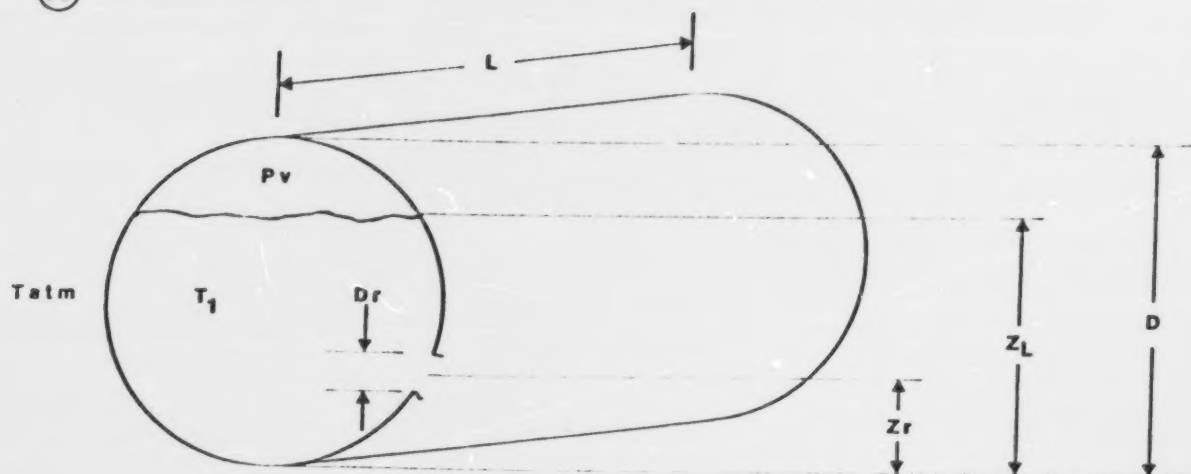
From Eqn. 1

$$\text{Eqn. 6} \quad \dot{M}_L = \frac{C_D A_R}{(1-\beta^4)^{1/2}} \left(2(P_1 - P_2) \rho_1 \right)^{1/2}$$

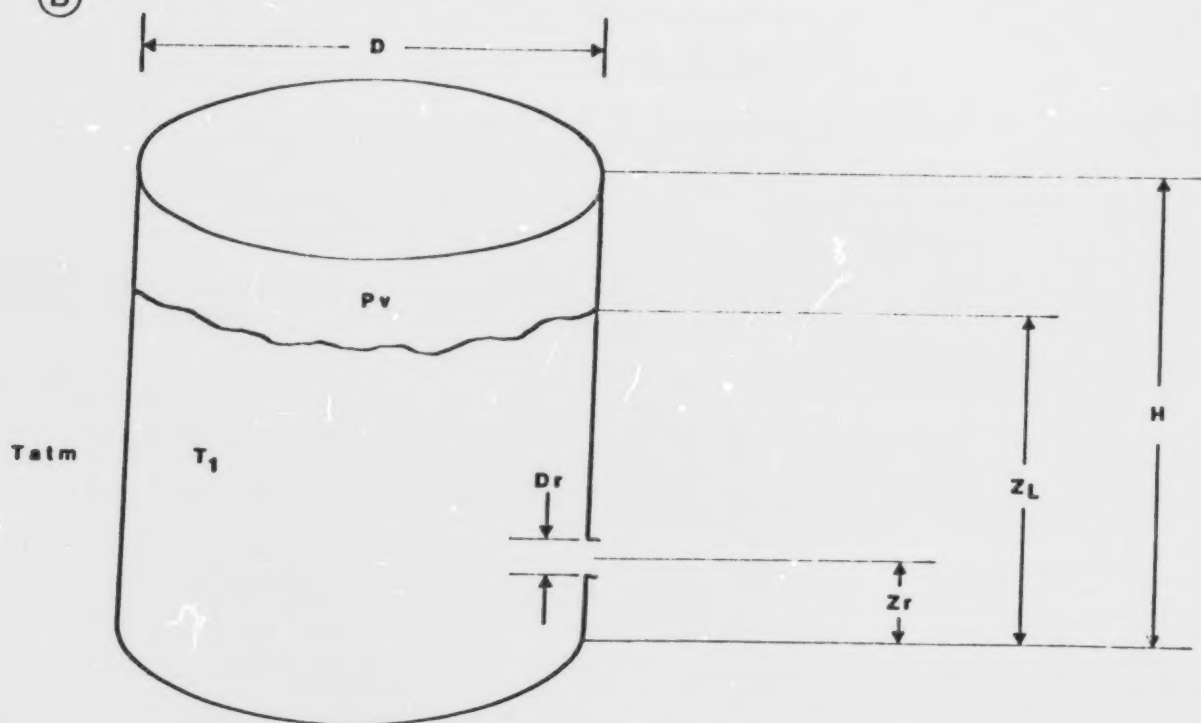
Now, $P_2 = P_{\text{atm}}$

FIGURE 1 TWO POSSIBLE TANK ORIENTATIONS

(A)



(B)



Eqn. 7
$$P_i = (Z_L - Z_R + D_R/2) \rho_l g + P_v$$

where: P_v = void space vapour pressure at T_1 (N/m^2)

Thus,

Eqn. 8
$$\dot{M}_L = \frac{C_D \rho_l A_R}{(1 - \beta^4)^{1/2}} \left(2(P_v - P_{atm})/\rho_l + g(Z_L - Z_R + D_R/2) \right)^{1/2}$$

if
$$P_v - P_{atm} + \rho_l g(Z_L - Z_R + D_R/2) \leq 0.01 P_{atm}.$$

Air will be ingested into the tank, permitting fluid to continue leaking at a rate controlled by A_p and the rise time of the bubble in the remaining liquid above the puncture^p (Dodge et al, 1980).

As Z_L decreases, P_v drops thus inducing the liquid to evaporate and increase P_v to $P_{sat'd}$, the saturated vapour pressure. This evaporation will result in cooling of the liquid which in turn initiates a flow of heat from the surroundings into the tank.

Experiments (Dodge et al, 1980) have shown that:

Eqn. 9
$$\dot{m}_e = \dot{m}_{e sat'd} - 1.9 (\dot{m}_{e sat'd})^{5/4} / (\rho_l A_L \sqrt{RT_1})^{1/4}$$

where: $\dot{m}_e$ = evaporation rate of liquid (Kg/s)
 $\dot{m}_{e sat'd}$ = evaporation rate required to maintain P_v at $P_{sat'd}$ at T_1

In order to calculate $\dot{m}_{e sat'd}$ a heat balance is undertaken:

Eqn. 10
$$q = \dot{m}_{e sat'd} \lambda = U_o A_o \Delta \bar{T}_L = \pi D^2 Z_L \rho_l C_p \Delta T$$

where: q = heat flux into container (J/s)
 U_o = overall heat transfer coefficient ($J/sm^2 \circ K$)
 A_o = overall heat transfer area (m^2)
 $\Delta \bar{T}_L$ = log mean temperature difference ($^{\circ}K$)
 C_p = heat capacity of liquid ($J/Kg^{\circ}K$)

Now,

$$\text{Eqn. 11} \quad U_o = \frac{1}{\frac{D_o}{D_i h_i} + \frac{x_w D_o}{K_m D_L} + \frac{1}{h_o}}$$

where: D_o, D_i = outside and inside diameters of tank (m)
 D_L = log mean diameter of tank (m)
 h_i, h_o = inside and outside local heat transfer coefficients ($\text{J/m}^2\text{s}^\circ\text{K}$)
 x_w = wall thickness (m)
 K_m = thermal conductivity of tank wall ($\text{J/m}^2\text{s}^\circ\text{K}$)

h_i is related to fluid and wall temperature, h_o is related to environmental and wall temperature (and wind speed etc.) and K_m can include insulating effects.

An iterative process combining expressions for h_i , h_o , 11 and 10 is used until the three right-hand quantities of equation 10 are equal. At this point T_1 is specified and,

$$\text{Eqn. 12} \quad \dot{m}_{e \text{ set'd}} = \frac{U_o A_o \overline{\Delta T_L}}{\lambda}$$

Substituting into 9 yields m_e ; now using the Clausius - Clapeyron equation;

$$\text{Eqn. 13} \quad \ln\left(\frac{P_y}{P_D}\right) = \lambda\left(\frac{1}{T_D} - \frac{1}{T_1}\right)/R$$

where: R = gas constant ($\text{J/Kg}^\circ\text{K}$)
 P_D = reference pressure (N/m^2)
 T_D = reference temperature ($^\circ\text{K}$)

P_y can be estimated.

The process is then repeated for the next time step. A simplified flow chart (Figure 2) illustrates the model. An example output, used to predict oil outflow rates from damaged ship cargo tanks is given in Figure 3 (S.L. Ross, 1983).

CONCLUSIONS

A mathematical model describing the fluid mechanics and heat and mass transfer associated with a leak in a chemical storage or transportation tank is being developed. A computer model is then being used to solve the complete set of governing equations under a wide range of conditions. An analysis of the sensitivity of the equations to simplifying assumptions will also be made to identify the key input parameters necessary to accurately predict release rate conditions. Results from the final model will be condensed into a new series of nomograms capable of predicting the outflow rate and duration of tank leakage incidents under a wide range of conditions.

FIGURE 2

LIQUID RELEASE MODEL FLOWCHART

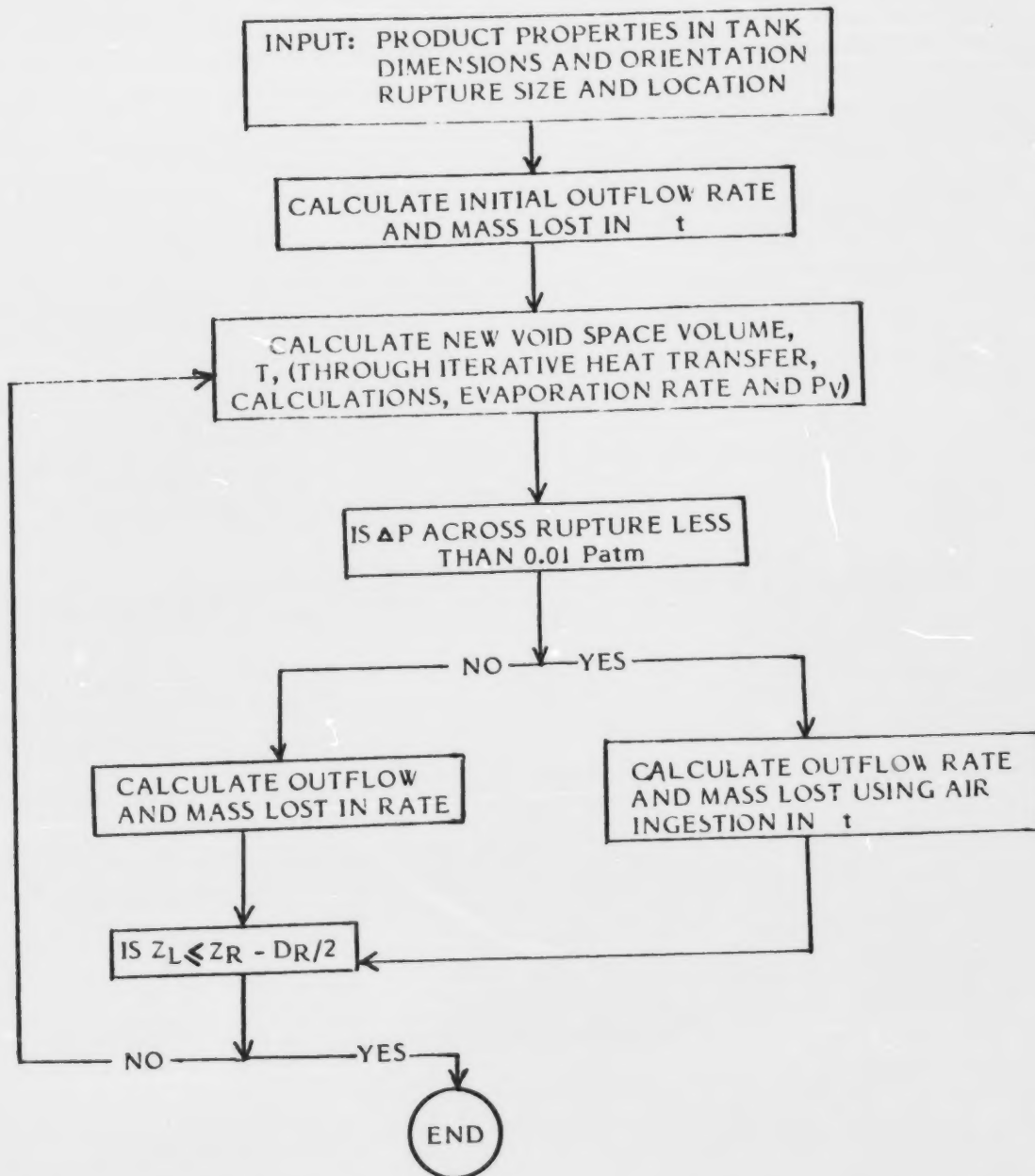
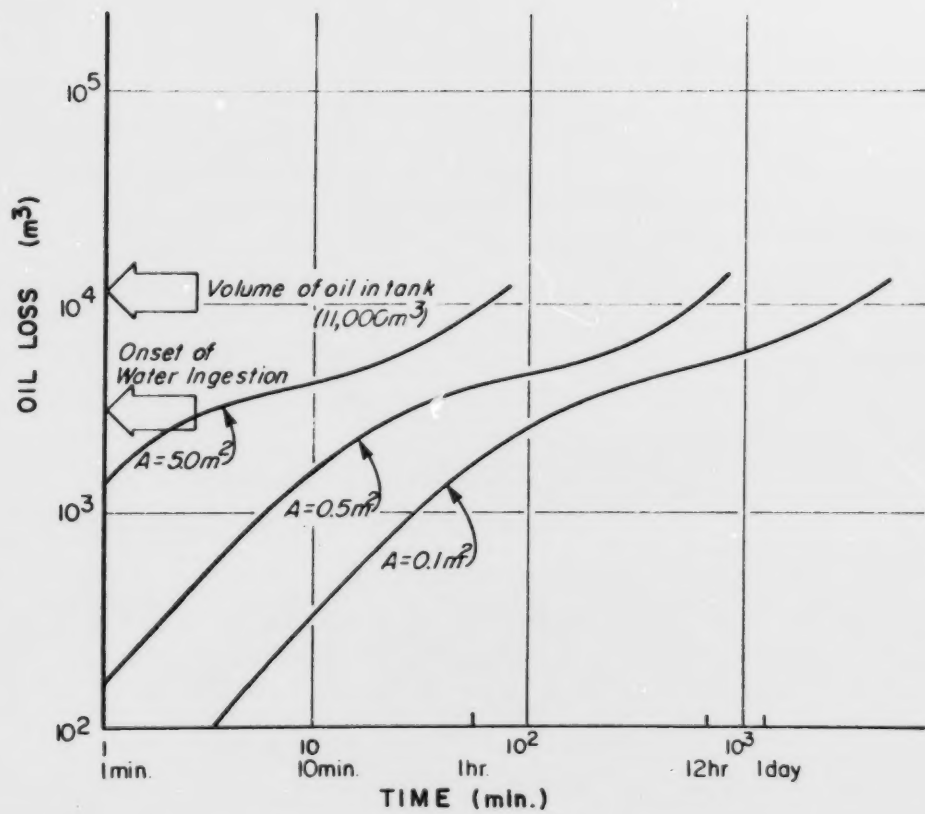


FIGURE 3

80,000 DWT TANKER · CARGO TANK OIL RELEASE

*Hole at Waterline**Tank Fully Vented*

REFERENCES

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ASSESSING THE IMPACT OF HAZARDOUS IMMISCIBLE LIQUIDS IN SOIL

G.J. Farquhar and E.A. McBean

University of Waterloo

November 1984

ABSTRACT

This paper describes the current status of research assessing the behavior of immiscible hazardous contaminants in soil. The work is supported in part by Provincial Lottery Funds and is being performed in the Department of Civil Engineering at the University of Waterloo.

A major portion of the research involves the simulation of immiscible liquid behavior in soil through the use of computer models. This includes (i) a model for spills onto soil with overland flow, penetration and evaporation, (ii) a model for the transport of immiscible liquids in soil either saturated or unsaturated, and (iii) a model for the movement of hazardous vapours in unsaturated soil.

Another area of research is experimental in nature but is only in its initial stages. It involves (i) the development of methods to detect immiscible liquids in soil through measurements of dielectric coefficients, thermal conductivity and electrical conductivity, and (ii) the performance of experiments to yield information on the flow of immiscible liquids in soil, especially the relationships between relative permeability, capillary pressure and percent saturation.

Research is also in progress to develop a spill response model which incorporates the behavior of the spilled liquid including overland flow, penetration, evaporation and transport within the soil and also recommends remedial action specific for the incident.

A literature review on the subject is near completion. It has approximately four-hundred references and was prepared with the assistance of a key-word information storage and retrieval system developed on a microprocessor for this research.

INTRODUCTION

In recent years, increased emphasis has been placed on hazardous materials spilled onto soil and the impact of these materials on the soil and groundwater environment. The transport of the contaminants, their interactions with the solid, aqueous and gaseous phases of the subsurface and the development of remedial measures have been areas of major research effort.

Immiscible liquids such as petroleum products and solvents are of special concern because many are defined as hazardous and all have the property of not mixing with water. This property adds greatly to the complexity of these contaminants as they penetrate the soil. Although the behavior of soil water is reasonably well understood, the behavior of multiphase fluids consisting perhaps of an aqueous phase, an immiscible liquid phase and a gas within a solid soil phase is not. It is because of this need for additional information together with the frequency and hazard of immiscible liquids spilled onto soil that this work was undertaken.

The research has been divided into four major sections comprised of:

1. Literature Review
2. Simulation Model Development
3. Experimentation
4. Spill Response System Development

The schedule for the research has been set for a three-year period, of which the first year is nearing completion. Funding has been provided by the Ontario Ministry of the Environment from Provincial

Lottery Funds and the Natural Sciences and Engineering Research Council.

This document is a progress report describing the work which has been accomplished to date.

LITERATURE REVIEW

To this point in the research, approximately 400 documents and papers related to hazardous immiscible liquids and their behavior when spilled onto soil have been reviewed. Two computer-based search systems WATMARS and AWWA were used to identify relevant information.

An information storage and retrieval package (ISRP) using the IBM DBASE II Software System was developed as a part of this work. The ISRP has the following characteristics.

1. Storage Format

This includes reference number, authors, title and publication data stored on 5-1/4" floppy disk.

2. Key Words

Each document is assigned up to 10 sets of key words from the list shown in Table 1.

3. Comment

A comment about the document and its content is stored on the disk.

4. Retrieval

The Users' Manual for the ISRP describes how the system is accessed through use of key words. The user is able to print out the author, title and comment for all documents stored with the key words entered.

The data stored can be added to or modified as more information is acquired.

A report describing the results of the literature review is in preparation. A first draft has been completed. The Table of Contents of the report is shown in Table 2.

SIMULATION MODEL DEVELOPMENT

Very little quantitative information is available on the behavior of hazardous immiscible liquids in soil. This applies to both field and laboratory investigations. It is especially the case for soil/contaminant interactions, relationships for permeabilities and capillary pressures for variably saturated, multifluid systems and the spreading and infiltration of spilled liquids onto soil. It also does not appear that this kind of quantitative data will be available in the near future. Consequently, it was decided that the development of mathematical simulation models should be a part of this research in order to study immiscible fluid behavior more extensively.

Mathematical models are simplified representations of physical phenomena. However, within the constraints of the underlying assumptions, these models can be used to examine a range of conditions which would not be feasible to investigate on an experimental basis. In this research it is also intended that a series of simulation models be linked together to encompass a complete spill including spilling, evaporation, penetration, transport in the unsaturated zone and transport on and in the zone of saturation. The models will ultimately be used both to learn about various spill conditions and to assess various remedial strategies.

At this point in the research, work has been done on three simulation models as discussed briefly below.

1. Spill Simulation Model (Wall, 1984)

The spill simulation model developed in this research takes account of two specific conditions;

- a. discharge from a source onto an inclined soil surface producing a hydraulic bore of spilled material moving down the slope (analogous to border irrigation), and
- b. discharge onto a horizontal soil surface creating an enlarging circular pool of spilled liquid.

In both cases, provision is made for variable liquid inflow, infiltration to the soil and evaporation into the atmosphere. The processes which govern spill formation have been expressed in the form of the St. Venant Equations with rectangular co-ordinates for condition "a" and polar co-ordinates for condition "b". These equations are nonlinear, nonhomogeneous, first order, hyperbolic partial differential equations. The system also accounts for supercritical and subcritical flow, a moving hydraulic jump and a moving bore. Because of the complexity of these equations, analytical solutions were not possible. Several approximate solution methods were examined in detail with the MacCormick explicit finite difference scheme proving to be satisfactory in most cases. The preservation of both mass and momentum and numerical dispersion were checked as solutions were generated by the model.

The spill of a viscous volatile liquid involves the dynamic interaction between forces which drive the liquid over the soil surface (momentum and pressure) and those which resist it (viscous and surface friction).

Resistance to overland flow controls the depth, the shape of the spill and the location of the hydraulic jump. Because of the presence of fluid turbulence, resistance to flow in this model was expressed in

terms of the Darcy-Weisbach relations with the introduction of a constant friction factor (Kincaid, 1970; Millel and Hornberger, 1979).

Infiltration of the liquid during spill formation is a complex system which depends on both capillary and gravity forces. The approach taken in this work is a simplification of the true system. A tubular configuration with both capillary and gravity components was used. Coefficients for the model must be determined experimentally.

Evaporation from the pool formed by the spill was represented as a mass transfer equation (Sutton, 1953; MacKay and Matsugu, 1973) adapted for southern Ontario conditions.

Other models have been developed to simulate a liquid spill but these were judged to be insufficient for this work. In most cases the authors failed to account for the energy in the inflow. Many, in fact, used an instantaneous spill with constant depth. Others omitted infiltration and evaporation from the analysis. The need for a more complete model structure was recognized.

The literature review associated with this study failed to locate existing data, from either field or laboratory experiments, for use in verifying this spill simulation model. Attempts will be made in the future to obtain or develop data on spill formation.

1.1 Test Simulations

A series of test spill simulations were performed with the model;

- a. to evaluate its overall performance, especially with respect to mass and momentum transport,
- b. to test the sensitivity of spill formation to model input parameters such as rate of inflow, soil roughness and infiltration rate, and,

c. to examine the spilling of various liquids under a range of conditions.

Two examples of the simulations performed are shown below.

Case 1

Case 1 simulated a slow spill of liquid from a long container, (perhaps a train tank car on its side) onto a sloping soil surface.

- flow $Q = 2.32 \times 10^{-3} \text{ m}^3/\text{s}$ per m of tank width
- soil slope(s) = $7.5 \times 10^{-4} \text{ m/m}$
- soil roughness (n) = $3 \times 10^{-2} \text{ m}^{1/6}$
- node spacing = $2 \times 10^{-2} \text{ m}$
- evaporation and infiltration were not considered.

The model used in this analysis was in the rectangular co-ordinates format because of the sloped surface. The output is shown in Figures 1, 2, and 3. Figure 1 shows the location on the liquid front (or moving bore) with respect to time. It must be noted that edge effects have been excluded from the model. Therefore, no lateral spreading of the liquid is accounted for, thus producing a rectangular-shaped spill. The simulation becomes a "worst case" in terms of spill length being longer but narrower than the real spill.

Figure 2 shows the fluid profile (depth vs. distance) at 5 time period up to 600 seconds and compares uniform and critical depths for the flow field (note vertical distortion). Figure 3 shows the velocity profile. It can be seen that, as expected, the spill depth increased with a corresponding reduced velocity as the spill distance increased. Both fluid mass and momentum were preserved. Since subcritical flow existed, no hydraulic jump was produced.

Case 2

Case 2 involved the spill of a liquid onto 3 flat surfaces consisting of asphalt (Case 2a), clay loam (Case 2b) and coarse sand (Case 2c). The source of the spill was assumed to be a ruptured container with volume of 62.5 m^3 , a rupture effective diameter of 0.4m and a discharge coefficient of 0.85. The decreasing flow produced from this configuration was $Q = 0.704 - 0.004t$ with t in seconds. A specific rate of infiltration was assigned to each soil (0 for asphalt and >0 for clay and sand). The ponded liquid evaporation rates were the same for each soil.

The model written in polar co-ordinates was used in this simulation to produce a circular pond with time increasing to 326 seconds.

Figure 4 shows the depth (note vertical distortion) profile for the spill on the asphalt surface. The relative locations of the spill front and the hydraulic jump are shown.

Figure 5 shows the location of the spill front and the hydraulic jump for the 3 surfaces with respect to time. The spill front on coarse sand actually retreats somewhat in response to the combined effects of decreasing flow, infiltration and evaporation.

Figure 6 shows the situation for the clay loam by comparing the total spilled volume with the ponded, infiltrated and evaporated volumes. By comparing Figures 5 and 6, it can be seen that the pond volume decreases although the pond diameter increases.

1.2 Summary

The results of the model testing to this point in the work indicate that it can produce realistic spill simulations in response to a variety of input conditions while conserving mass and momentum. Additional work will be done in the future (1) to streamline the model to reduce

computational time, (2) to validate it if actual spill data can be found or developed and (3) to incorporate the model into a spill response model.

2. Immiscible Liquid Porous Media Flow Model (Osborne, 1984)

The purpose of this work was to create a model to simulate the flow of immiscible liquids through porous media after introduction to the soil either from a spill or through direct disposal. While the model has been essentially completed, linkage between it and the spill simulation model has yet to be attempted.

Mathematical simulation of two-phase flow in porous media has been used in the petroleum industry for some time to analyze the behavior of gas and oil in reservoirs, and to optimize the effects of steam- and water- flooding. Various numerical techniques, including the finite-difference and finite-element methods have been used to solve the immiscible displacement equation. However, application of such numerical models to immiscible groundwater contamination problems is a relatively new practice.

In this work, a two-dimensional, two-phase mathematical model was developed, based on Darcy's law and conservation of mass for each liquid. The result was a pair of coupled, nonlinear partial differential equations which display both parabolic and hyperbolic characteristics, depending on the magnitude of a nonlinear coefficient.

A numerical model was developed to solve the equations using a generalized method of weighted residuals in conjunction with the finite-element method and linear quadratic isoparametric elements. To alleviate numerical difficulties associated with hyperbolic equations, upstream weighting of the spatial terms in the model was incorporated.

The theoretical and numerical accuracy of the model was verified by comparison with simulation results with those from an existing one-dimensional finite difference two-phase flow simulator (Little, Arthur D. Inc. 1983). This form of verification was necessitated by the lack of actual data on immiscible liquid transport in soil.

One of the comparisons made involved a vertical column of soil 7.0m in length and consisting of the 3 soil components shown in Figure 7. The initial distribution of non-aqueous phase liquid (NAPL) is also shown plotted as elevation against % NAPL saturation (S_m) within the zone of saturation. Relationships between relative permeability (k_r), capillary pressure (P_c) and % wetting fluid saturation (S_w) were the same for both models. However, the model developed here is not equipped for hysteretic functions since its intended application is for the first time displacement of water by the immiscible liquid. Thus, only the primary drainage curve was used.

Figures 7 also shows comparisons between the NAPL profiles predicted by the two models. The agreement was thought to be reasonably good and was therefore taken as evidence that the model developed in this work was performing in a satisfactory way.

The finite-element model was then used to simulate the migration of an immiscible organic solvent in groundwater, from a chemical waste dispersal site located north of Niagara Falls, New York. The effects of uncertainty regarding several of the liquid and porous media properties were examined, and it was concluded that the value of the model was limited less by the numerical approximations involved than by the accuracy of input parameter estimations. The results of this simulation are presented in the work of Osborne (Osborne, 1984).

3. Vapour Transport Model

At locations where volatile liquids have been spilled or have migrated away from disposal sites, concern often arises over the hazards resulting from the vapours produced at the liquid interface. Both experimental and theoretical work are being used to study this problem. The experimental work is discussed subsequently. The theoretical work will involve the development of a vapour transport model for soil environments.

The vapour transport model has not yet been developed but will be based on an existing model created by the authors to simulate the movement of methane (CH_4) gas through soil from landfill sites (Metcalf, 1982; Farquhar and Metcalf, 1982). The model is based on equations for continuity and flow in two dimensions.

The flow or connective equation is the Darcy Equation. Estimates of gas conductivity in variably saturated soil were used (Bear, 1972). The continuity equations accounted for dispersion, convection and loss terms. Gas diffusion in porous media, dispersion, dissolving from gas into liquid phase and density differences between gases were taken into account. Discharge of gases at the soil surface was simulated using transport equations for a laminar sub-layer (Thibodeaux, 1979).

The CH_4 transport model was tested using data collected at two locations, the Mississauga Landfill and the Ottawa Street Landfill in Kitchener, Ontario. The results from the Mississauga test are briefly discussed below.

A plan view of the Mississauga Site is presented in Figure 8. The location of a pumped (vacuum) gas venting system along the one side of the landfill is shown as are the locations of piezometers in a line perpendicular to the edge of the landfill. During the Fall of 1980, the

venting system was shut off for 85 days to permit landfill gas to migrate outward into the adjacent soils. Gas pressures and concentrations were measured at the piezometer locations during this period.

A summarized soil profile along the piezometer line is shown in Figure 9. The progression of CH_4 with time away from the landfill is shown in Figure 9, 10 and 11 as CH_4 percentiles (by volume) plotted vs. time. The model simulations are also shown and indicate reasonably good agreement between the actual and simulated concentrations. These encouraging results support the extension of the model to simulate vapour movement in soil.

EXPERIMENTATION

A series of experiments has been proposed for this study (a) to examine the movement of immiscible liquids and their vapours in soil and, (b) to provide data for the verification of numerical transport models. Work is just beginning on these experiments. The information presented here provides a brief description of the anticipated research programme.

Liquid Infiltration

Experiments will be conducted to study the infiltration of immiscible liquids into sand either partially or fully saturated with water. A major difficulty with this work is the measurement of the relative concentration of the wetting and non-wetting phases during transport through the soil. In situ measurements of electrical (EC) and thermal (TC) conductivity and dielectric coefficients (DC) have been proposed. To this point in the research static measurements of DC for various soil - liquid mixtures have been completed. Figure 12 shows some results using sand with different amounts of water, mineral oil

(floater) and carbontetrachloride (sinker). The DC shows good separation between water and the immiscible liquids at equivalent concentrations.

It should serve as a means for distinguishing between liquids. For a specific liquid, the data in Figure 13 show that capacitance (from which DC is calculated) responds well to changes in concentration. This property of the measurement will be necessary in order to detect the dispersed front of an immiscible liquid moving into a water-wetted soil. In situ measurements of DC have not yet been attempted in this work but have been done successfully elsewhere (Alharthy and Lange, 1984). Experiments to quantify the relationships between relative permeability, capillary pressure and percent liquid saturation are of major interest and will be attempted in this work. Experimentation along the lines of that used in the oil industry will be used for several immiscible liquids.

Vapour Transport

Experiments will be conducted to trace the movement of vapours in soil. Soil columns will be exposed to volatile immiscible liquids either as pools of liquid at the base of the soil or as zones of unsaturated, liquid-contaminated soils from which vapours can emanate. Gas chromatography will be used to measure vapour concentrations in the gas phase and will serve to quantify rates of vapour transport.

SPILL RESPONSE SYSTEM DEVELOPMENT

An important result of this work will be the development of a Spill Response System (SRS) for immiscible liquids. Although emergency response models for hazardous wastes do exist, none is specifically and adequately designed for immiscible liquids spilled onto soil.

It is proposed that the SRS consist of a computer programme which integrates and interfaces component models currently under development;

- Spill Simulation Model
- Immiscible Liquid Porous Media Flow Model
- Vapour Transport Model

The SRS will function by simulating the sequential behavior of the liquid including: spill formation, infiltration, transport under variable saturation, retention in the soil and evaporation. Input information will be required for liquid properties and data on the spill conditions, data on soil surface conditions, site hydrogeology, climatic conditions and local land use conditions. Experience with modelling fluid behavior in soil has often shown that the accuracy of simulations is controlled by the quality of the input data for the subsurface soil conditions. At the time of a spill, data available at a site are likely to be sparse. Because of this, the SRS will contain default information that can be used to provide crude estimates of behavior until better data become available. In many cases, it is expected that certain conditions such as soil surface slope, liquid volatility, liquid density and viscosity, depth to groundwater and the presence of coarse soils will have a dominant effect on the simulation. This will then pre-empt specific components of the SRS and allow attention to be focussed on the

essential components. This would assist in the design of site instrumentation. In addition, components of the model can be helpful long after the spill occurred, to trace the movement of immiscible liquids in soil as an aid to site remedial work. Work on the SRS is in its initial stages.

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Table 1. Key Words for the Information Storage
and Retrieval Package (ISRP)

1.0 Monitoring, Testing, and Detection

- 1.1 Vapours in Air
- 1.2 Detection in Soil
 - 1.2.1 Vapours - In soil
- 1.3 Groundwater Analysis
- 1.4 Remote Sensing
- 1.5 Chromatographic Methods
- 1.6 Dielectric Coefficient; Conductivities
- 1.7 Geophysical Methods
- 1.8 Ultrasonification

2.0 Spill Behavior

- 2.1 Chemical Characteristics
- 2.2 Evaporation
- 2.3 Interaction With Hydrogeologic Materials
 - 2.3.1 Migration and Transport
 - 2.3.2 Attenuation
 - 2.3.3 Reactions

3.0 Remedial Work

- 3.1 Liquid Recovery
 - 3.1.1 Pumping
 - 3.1.2 Drainage
 - 3.1.3 Treatment
- 3.2 In Situ Treatment
- 3.3 Excavation
 - 3.3.1 Disposal
 - 3.3.2 Restoration
- 3.4 Encapsulation
- 3.5 Vapour Control

4.0 Models

- 4.1 Transport
 - 4.1.1 Saturated Soil
 - 4.1.2 Unsaturated Soil
- 4.2 Evaporation
 - 4.2.1 From Spills
 - 4.2.2 From Soils
- 4.3 Spilling
- 4.4 Vapours

5.0 Spill Management

- 5.1 Chemical Usage
- 5.2 Management Models
 - 5.2.1 General Guide-
lines
- 5.3 Legal Restrictions
 - 5.3.1 Government
Regulations
- 5.4 Safety
 - 5.4.1 Equipment and
Procedures

6.0 Field Studies

- 6.1 Simulated
- 6.2 Actual

7.0 Lab Studies

Table 2. Assessing The Impact of Hazardous Immiscible Liquids
On Soil and Groundwater: A Literature Review.
Table of Contents.

- 1.0 Monitoring, Testing, and Detection
 - 1.1 Vapour Phase
 - 1.1.1 Atmosphere
 - 1.1.2 Subsurface
 - 1.2 Drilling and Sampling
 - 1.2.1 Sample Analysis
 - 1.3 Chromatography
 - 1.3.1 Theory
 - 1.3.2 Application
 - 1.4 Surface Geophysical Methods
 - 1.4.1 Spill Monitoring
 - 1.5 Aerial Remote Sensing
- 2.0 Spill Contaminant Migration
 - 2.1 Attenuation
 - 2.1.1 Effects of Organic Liquids on Soils
 - 2.2 Vadose Zone
 - 2.3 Capillary Zone
 - 2.4 Saturated Zone
- 3.0 Remedial Work
 - 3.1 Hydrodynamic Control
 - 3.1.1 Migration Control and Contaminant Removal
 - 3.1.2 Treatment Methods for Fluids Extracted
 - 3.2 In Situ Methods for Treatment and Control
 - 3.3 Excavation, Transport and Control
 - 3.4 Encapsulation
 - 3.5 Vapour Control
- 4.0 Models
 - 4.1 Liquid Transport
 - 4.1.1 Applications
 - 4.2 Vapour Transport
- 5.0 Spill Management
 - 5.1 Chemical Usage
 - 5.2 Management Models
 - 5.3 Legal Restrictions
 - 5.4 Safety Considerations
 - 5.4.1 Equipment
- 6.0 Suggested Further Research

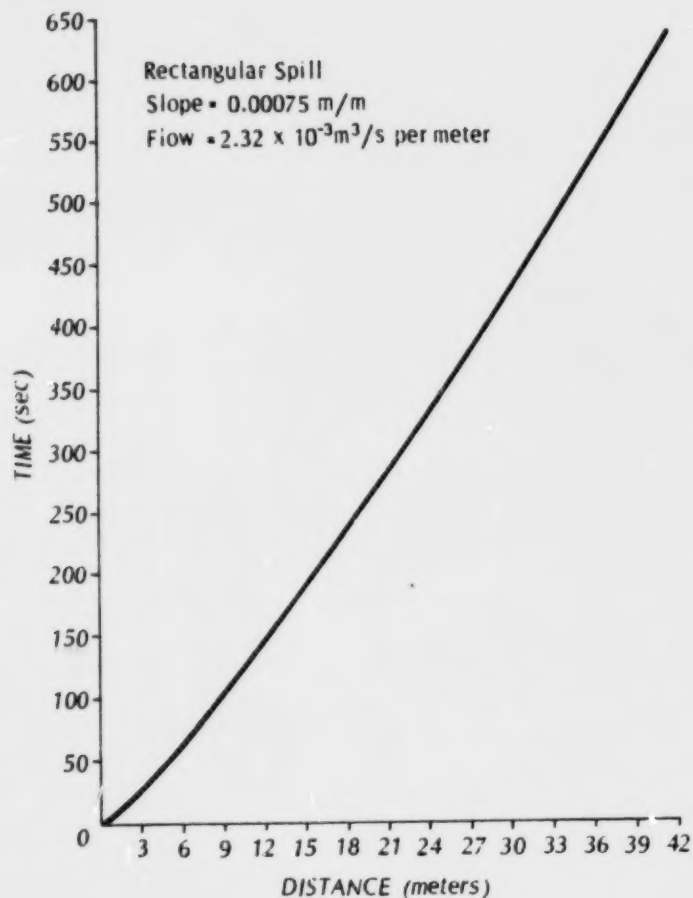


Fig.1- Location of the Spill Front with Time

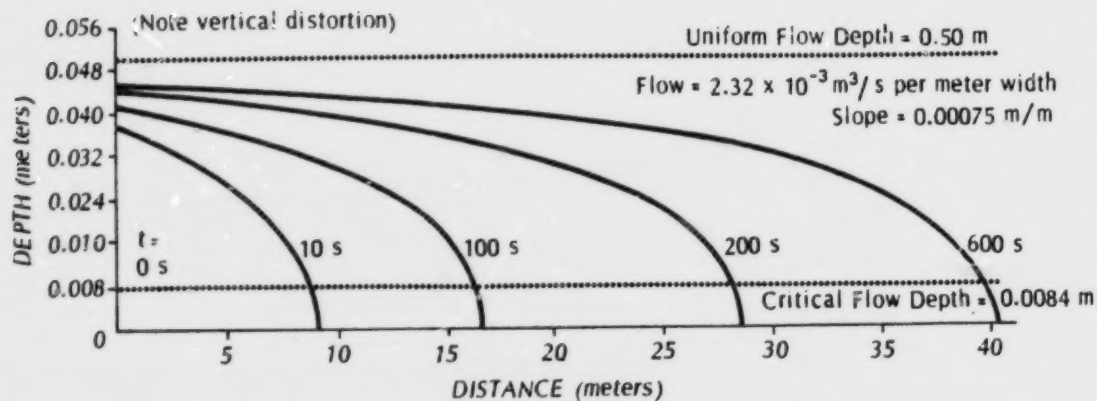


Fig.2- Depth Profile for Spill with Time

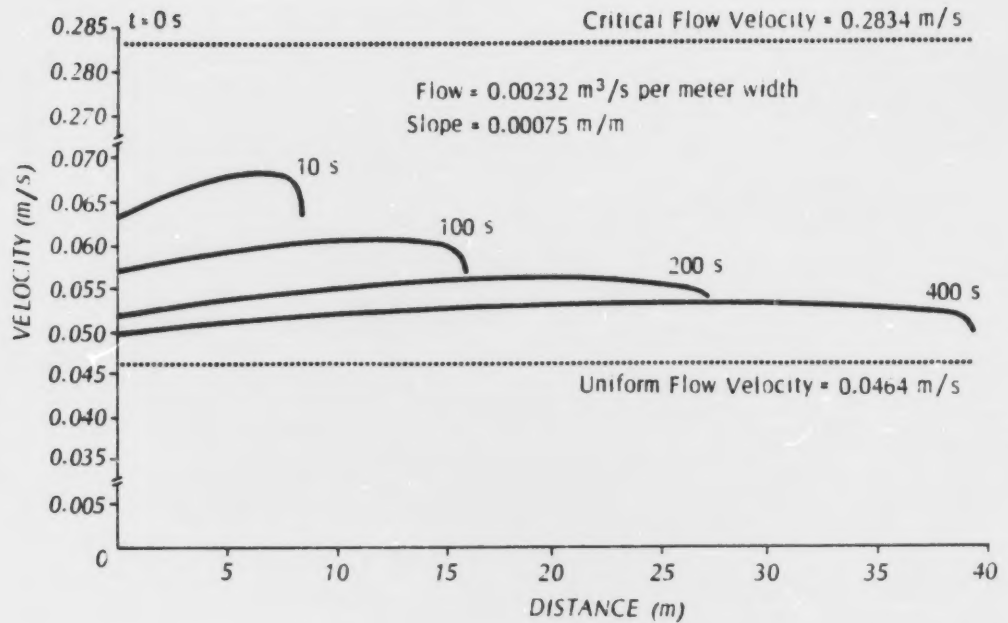


Fig.3 - Velocity Profile for Spill

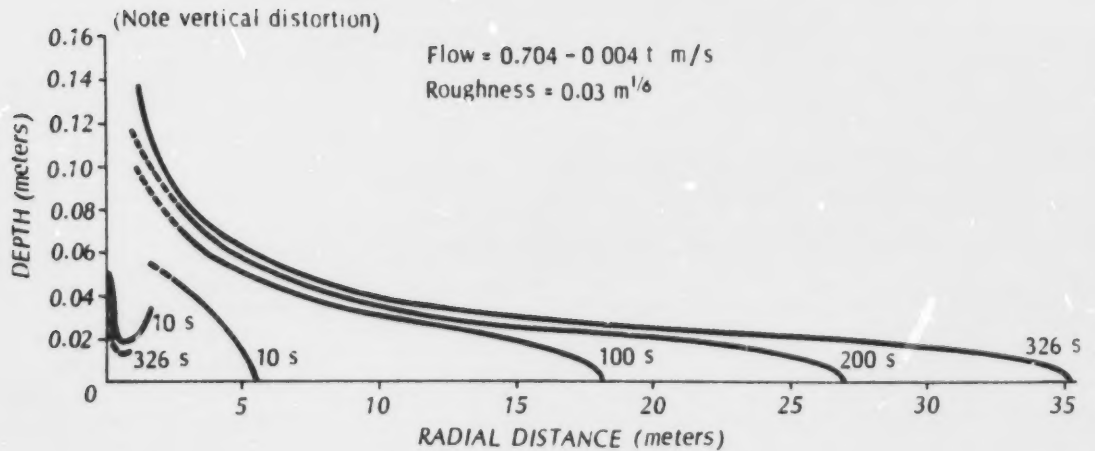


Fig.4 - Depth Profile for Radial Spill on to Flat Impervious Surface

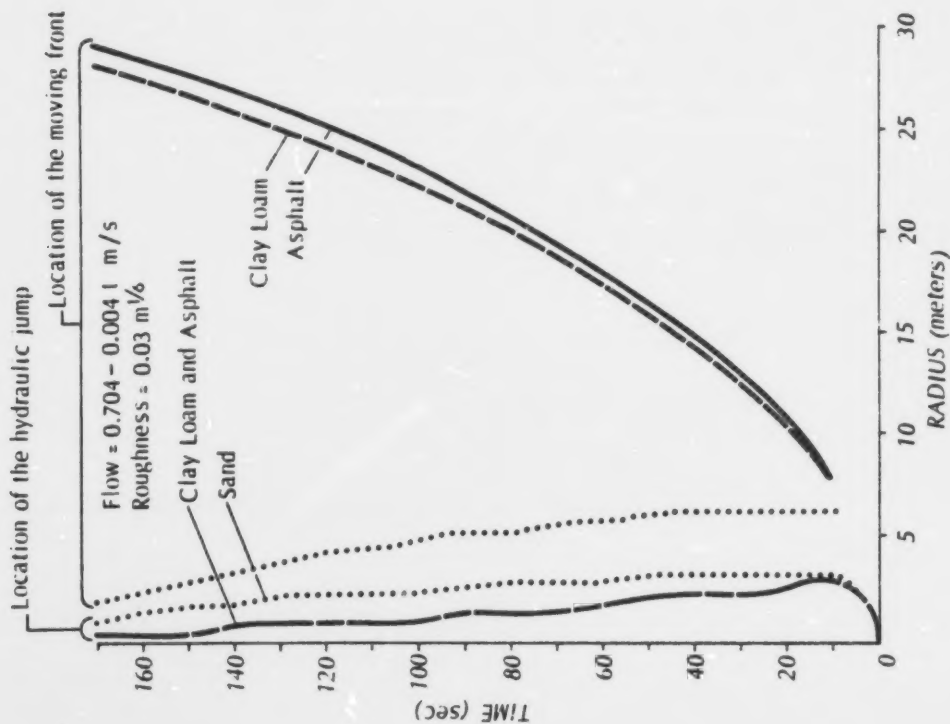


Fig. 5 - Location of the Hydraulic Jump and Moving Front

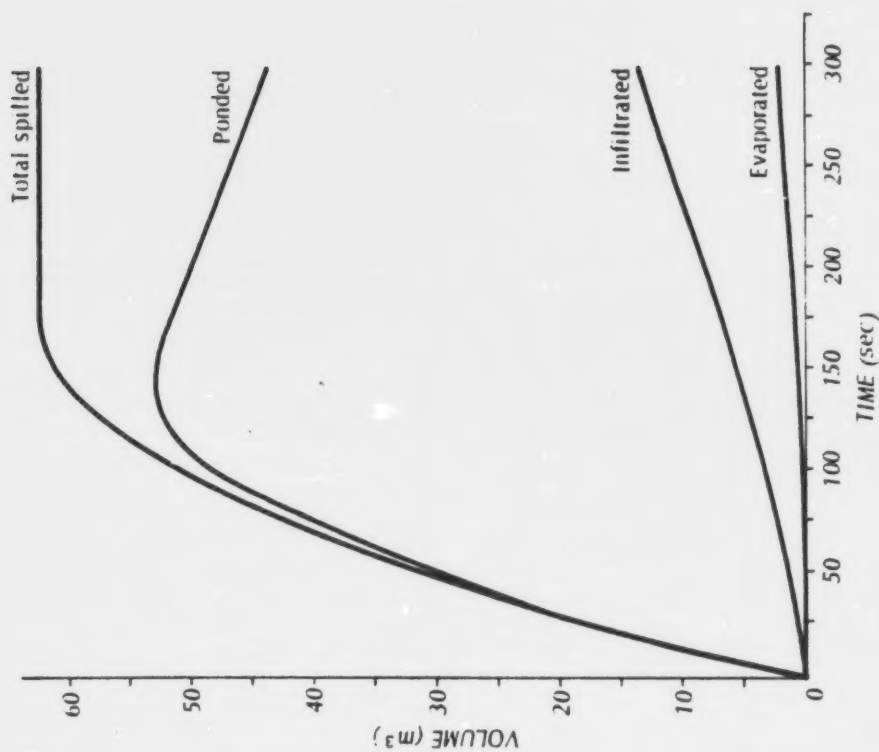


Fig. 6 - Accumulated Volume Distribution for Spill on to Clay Loam

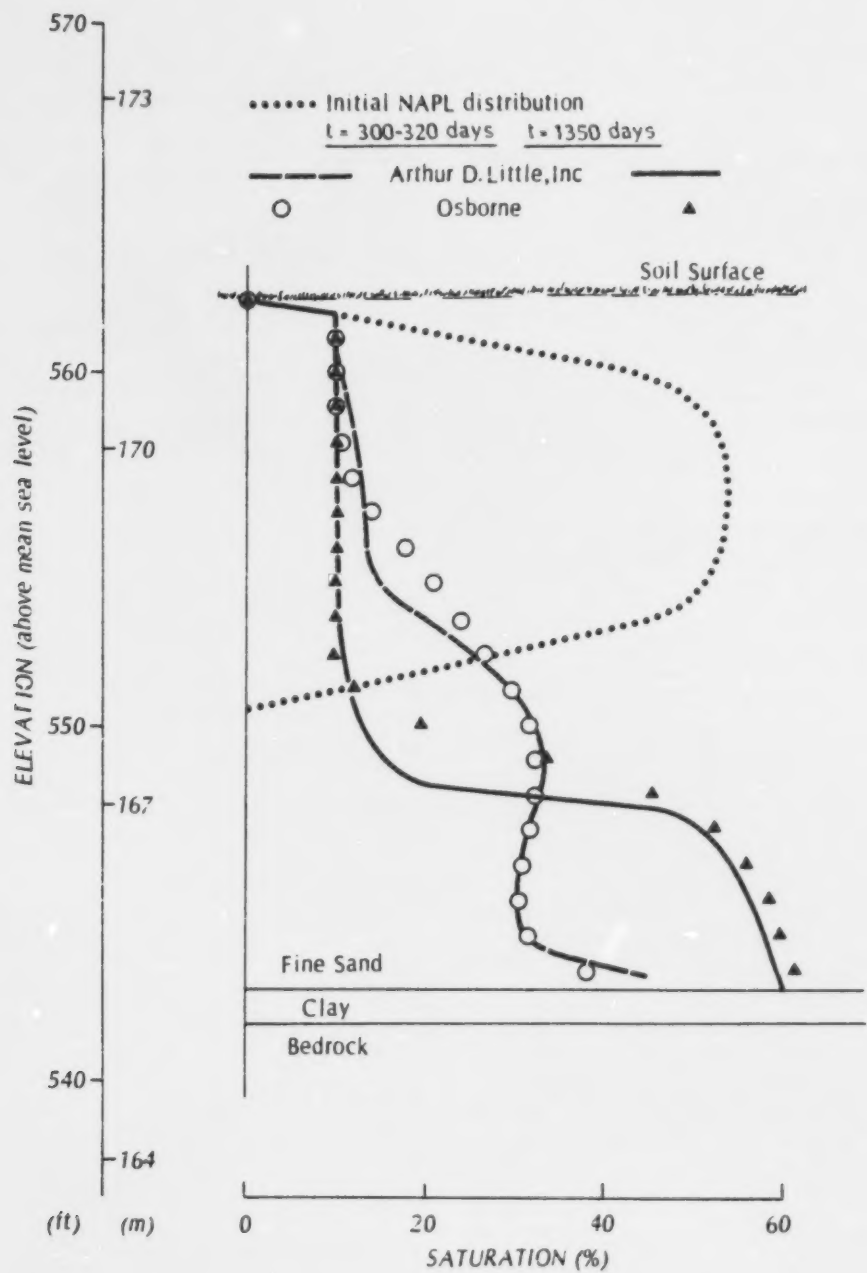


Fig.7-Lithology and NAPL Saturation Profiles (Osborne,1984)

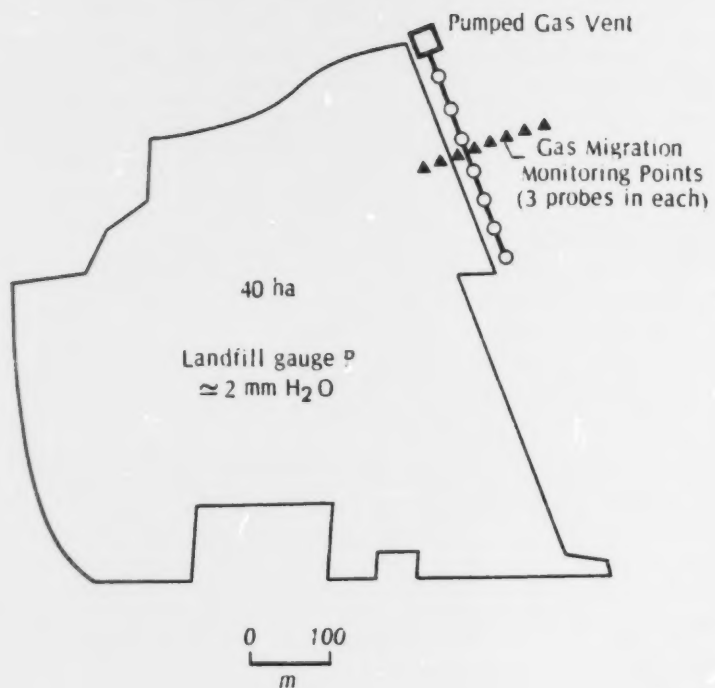


Fig.8- Monitoring CH_4 Migration at the Mississauga Landfill Site

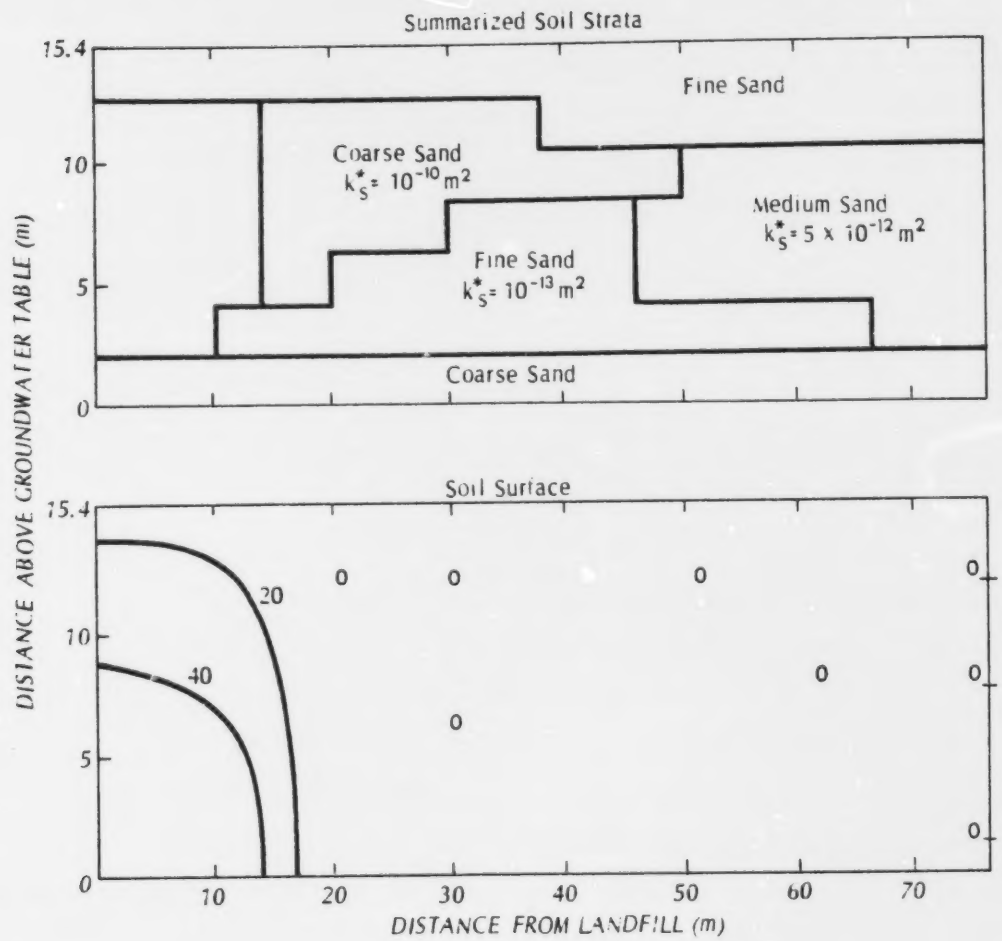


Fig.9-Methane Migration after Two Days at Mississauga

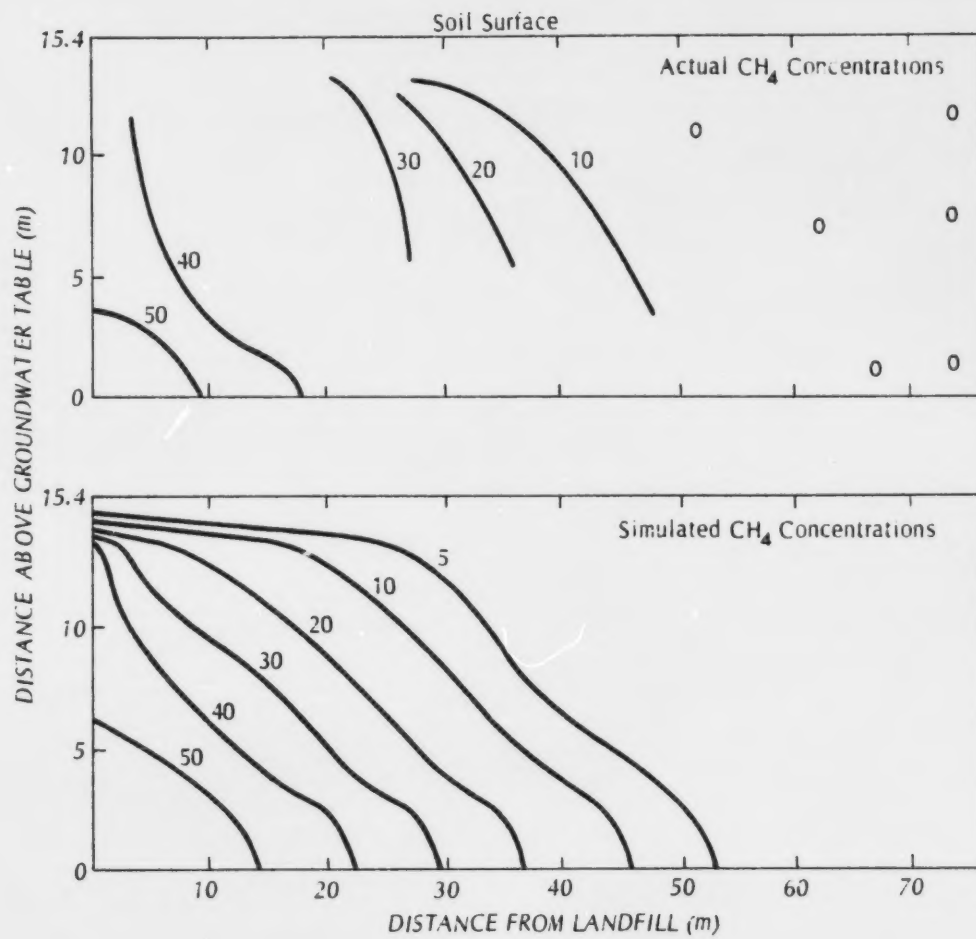


Fig.10-Methane Migration after 41 Days at Mississauga

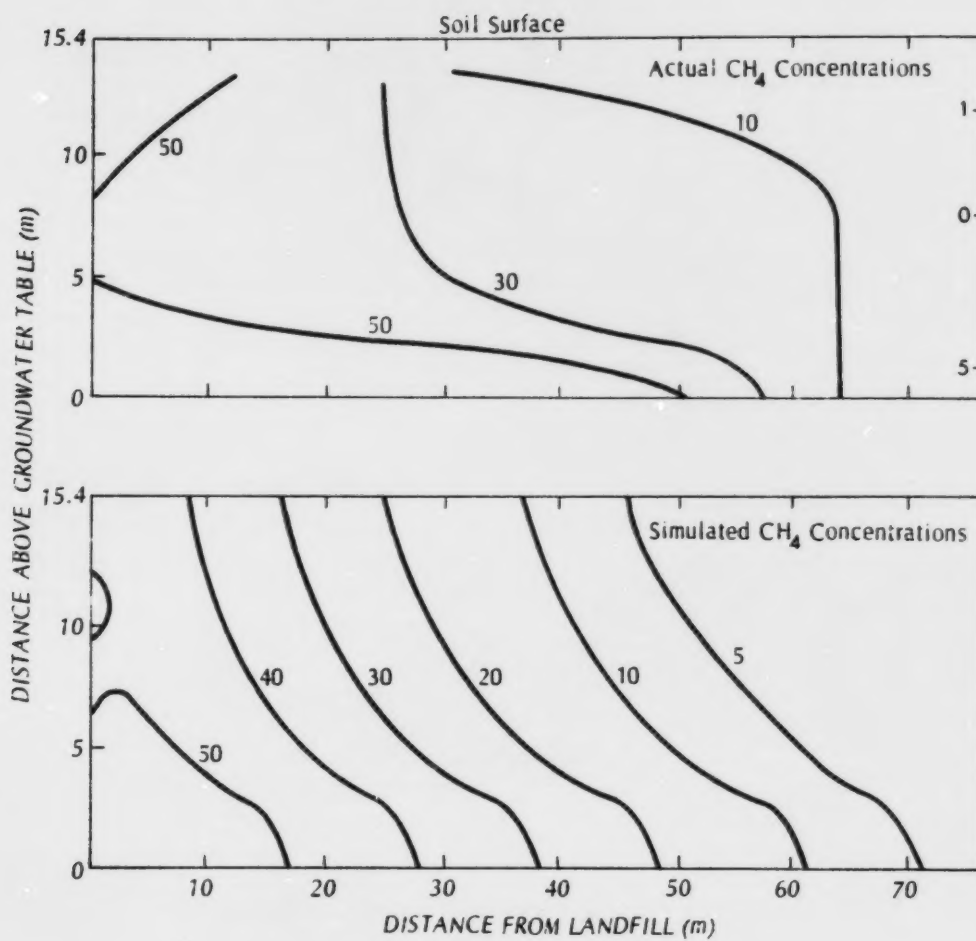


Fig.11- Methane Migration after 85 Days at Mississauga

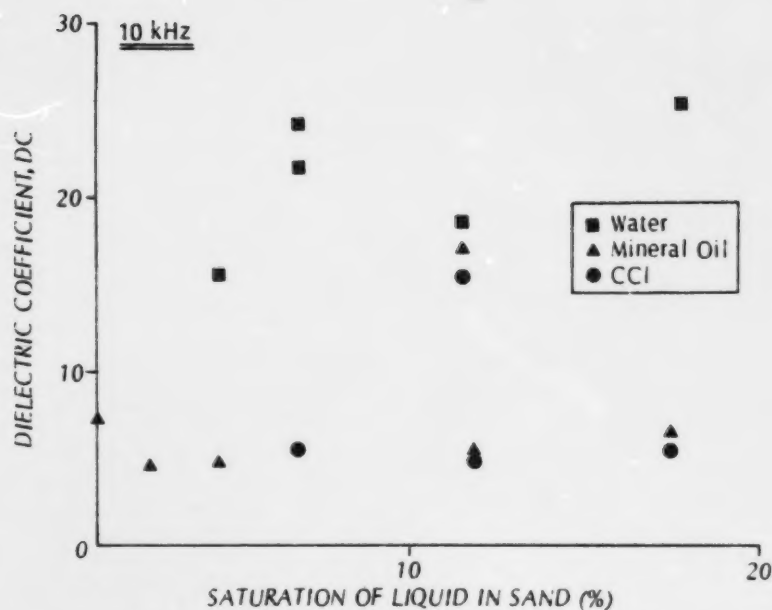


Fig.12-Measurement of Dielectric Constant for Various Soil-Liquid Mixtures

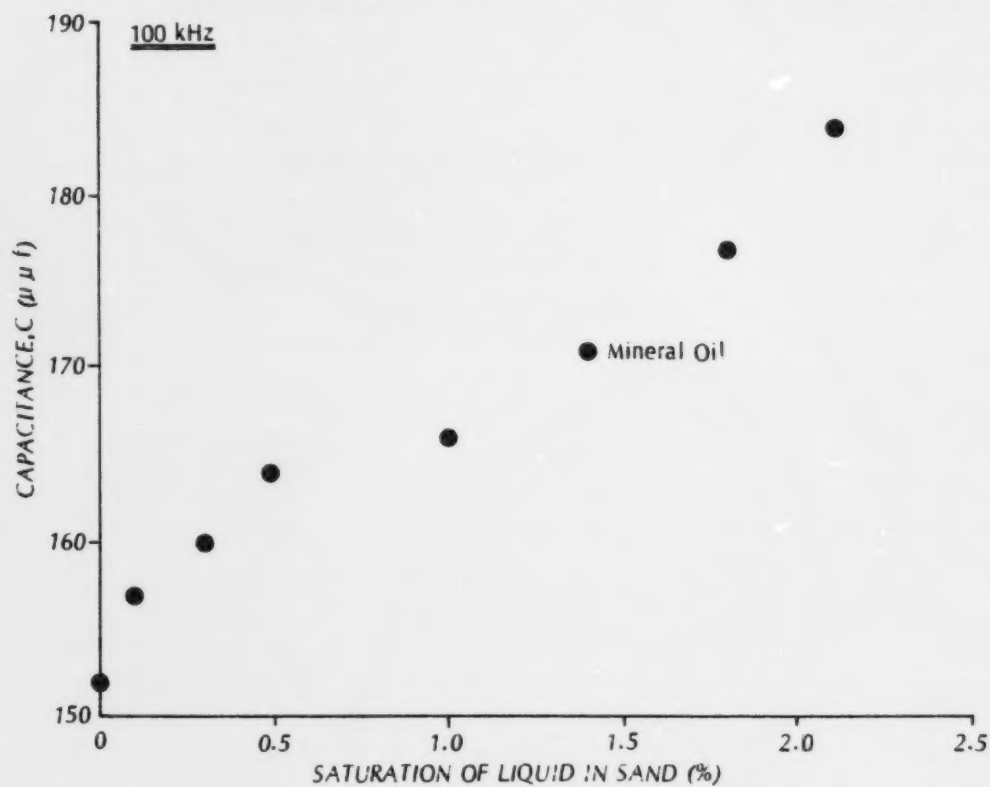


Fig.13-Changes in Capacitance with Increasing Liquid Concentrations in Soil

THE EVAPORATION OF VOLATILE LIQUIDS

P Kawamura
D Mackay

Department of Chemical Engineering and Applied Chemistry
University of Toronto

ABSTRACT

Two evaporation models have been developed and are currently being tested which estimate the evaporation rate of volatile as well as non-volatile liquids resulting from ground spills. Both models are based on steady state heat balances of the chemical pool and include effects of variables such as solar insolation and evaporative cooling. The simpler of the two, called the direct evaporation method, estimates the evaporation rate directly from available physical-chemical data. The second model, called the surface temperature method, determines the surface temperature of the evaporating pool by an iterative procedure. This temperature is then used to predict the evaporation rate. These two procedures are presently being compared with experimental data for verification.

INTRODUCTION

Accidental spills of hazardous and toxic chemicals during storage and transportation present a serious risk to the public's safety and to the environment. In particular, generation of excessive chemical vapour concentrations downwind of the accident may cause health problems and constitute a fire hazard, if the chemical is flammable. To establish the likely exposure concentration to the public and the possible effects on the the environment, the evaporation rate of the chemical must be determined. This study is concerned with the prediction of the evaporation rate of pure liquid chemicals resulting from ground spills with particular emphasis on volatile liquids.

The prediction of the evaporation rate will determine the approximate time required for complete evaporation, given the initial spill volume. The knowledge of this period and the evaporation rate, along with the physical properties of the chemical, is necessary to implement proper mitigative procedures in an event of a spill, such as the need (if any) for an immediate clean-up of the spill, and the possible evacuation distances. For example, if a relatively small amount of the chemical was spilled and was found to evaporate at a fast rate, it may be best to allow the chemical to evaporate to completion. Under these circumstances, evacuation may be necessary, depending on the evaporation rate (source strength), atmospheric conditions and the toxicity of the chemical. On the other hand, if a spill involving large amounts of chemical was found to evaporate at a slow rate such that the time required for complete evaporation is long, it may be best to proceed with appropriate clean-up procedures. Therefore, the estimation of the evaporation rate under various spill conditions is essential in dealing with spills of hazardous or toxic substances.

The evaporation rate is dependent primarily on the vapour pressure of the chemical, evaluated at the surface of the chemical pool, and the evaporation mass transfer coefficient. Mackay and Matsugu (1973) have determined this coefficient as a function of the wind speed, the diameter of the pool and the chemical's Schmidt number. However, evaluating the vapour pressure of the chemical, which is the evaporation driving force, requires a knowledge of the surface temperature of the evaporating pool.

This surface temperature is difficult to estimate since it is a function of many variables, including solar insolation, evaporative cooling and sensible heat transfer between the pool surface and the air, and between the pool and the ground. In general, the pool surface is lower than the average pool temperature, and the average pool temperature may be higher or lower than the air temperature. These differences may be small for relatively involatile chemicals but can become significant when dealing with chemicals of high volatility.

Highly volatile chemicals, such as pentane and methanol, due to their high evaporation rate, have a large evaporative cooling effect. This results in lower surface and pool temperatures, relative to air temperature. This phenomenon is called the "wet bulb effect". On the other hand, moderately volatile chemicals, such as toluene, may have surface temperatures greater or less than the air temperature. The magnitude of the temperature depression or increment depends on the energy exchange between the pool and the environment. Thus, prevailing environmental conditions, as well as the physical-chemical properties of the chemical must be combined quantitatively to evaluate the surface temperature.

Models of evaporation rate of chemicals from ground spills have been developed by several workers. Three such models, the US Army (1982), ESL (1983), and AWS (1978), predict the steady state evaporation rate by a simple formula based on mass transfer theory. Other models, such as the Shell model (1980), is an unsteady state computer model which estimates the evaporation rate of a spill as well as the downwind concentration of vapours as a function of time and distance. A relatively complicated computer model developed by Ille and Springer (1978, 1983) estimates the steady state evaporation rate of the hydrazine family propellants which includes the effects of solar radiation, ground roughness and terrain and evaporative cooling. Recently, Stiver and Mackay (1984) identified two key variables, the Henry's Constant and a term called the evaporative exposure, which enable the evaporation rate and the spill duration to be calculated.

However, these models are either too simple, or too complicated for use under actual spill conditions. The models employing the simple formula based on mass transfer theory assumes that pool temperature equals air temperature in calculating the vapour pressure. This assumption is not valid for volatile chemicals. The Shell model and Stiver's study neglect key variables such as solar insolation and evaporative cooling. The Ille and Springer model, (as well as the Shell model) are too complicated for use under field conditions since they employ a long computer program. A further drawback of the Ille and Springer model is that input parameters required are not generally available, thus limiting the applicability of the model to hydrazine propellants.

Therefore, it is desirable to develop a simple formula or procedure which can reasonably predict the evaporation rate of pure liquid chemicals resulting from ground spills under various environmental conditions. Critical parameters, such as solar insolation and evaporative cooling must be included in the formulation procedure. The purpose of this study is the development of such a formula or procedure and its verification with actual experimental data.

THEORETICAL PRINCIPLES

An energy balance for a chemical pool under environmental conditions may be written in the following form:

$$Q_{sol} + Q_{atm} - Q_{sur} - Q_{ev} - Q_{sen} + Q_{ext} = Q_t \quad (1)$$

in which Q_t is the increase in energy stored in the pool, Q_{sol} is the net solar radiation (corrected for the amount reflected from the surface), Q_{atm} is the long-wave radiation from the atmosphere absorbed by the pool, Q_{sur} is the long-wave radiation emitted by the pool, Q_{ev} is the energy lost by evaporation, Q_{sen} is the sensible heat exchange between the pool and the atmosphere, and Q_{ext} is any other source of energy into the pool. The units are $\text{kJ/m}^2 \text{ hr}$ for all terms. These terms are illustrated in figure 1 and are discussed in the following paragraphs.

1. Solar Radiation

Estimating the effective solar radiation on a horizontal surface of the pool involves determining the difference between the total incident and reflected solar radiation as a function of cloud cover and solar altitude.

Solar altitude, or angular elevation above the horizon, is a function of the latitude, declination of the sun, and the hour angle of the sun. These terms are related by the following expression which enables solar altitude to be calculated for any hour of any day of the year:

$$\sin a = \sin \phi \sin \delta + \cos \phi \cos \delta \cos h \quad (2)$$

where a is the solar altitude, in degrees; ϕ is the latitude, in degrees; δ is the declination, in degrees; and h is the hour angle of the sun, in degrees. The declination of the sun may be determined for any given day from a current solar ephemeris. However, reasonable accuracy is obtained from one table that lists the declination for any year since declination of the sun varies only by a few minutes from year to year on corresponding dates (Raphael, 1962).

The hour angle of the sun, which is the hour from solar noon converted into degrees, is calculated by the following expressions:

$$h = (12 - t_{as}) 360/24 \quad (3)$$

where:

$$t_{as} = t_1 + t_z - L/15 + EQ/60 \quad (4)$$

in which t_{as} is the apparent solar time, in hours; t_1 is the

local standard time, in hours; t_z is the time zone factor; L is the longitude, positive for locations east of the prime meridian and negative for west, in degrees; and EQ is the equation of time, in minutes. The equation of time, similar to declination, varies from day to day during the year but one table may be used for any year for engineering calculations. Therefore, the solar altitude can be determined for any location at any time of the year.

Raphael has gathered standard radiation curves from various sources and plotted the net solar insolation on a horizontal surface as a function of cloud cover and solar altitude, which is presented in figure 2. The net insolation is the difference between the total solar radiation (including diffuse and reflected sky radiation) and the reflected short-wave radiation from the surface of the pool. The reflective property was based on information obtained from the water surface.

Since reflectivities of most chemicals are unknown, the reflectivity of water may be used to approximate the reflectivity of most chemicals. Hooper (1984) states that the human eye is a good detector of the reflectivity of a material. Since most liquid chemicals are clear and have similar visual appearance as that of water, this approximation will be used for this study. Figure 2 can thus be used to estimate the net solar insolation incident on the surface of the spill.

2. Long-Wave Energy Exchange

Long-wave energy exchange involves the long-wave radiation from the atmosphere, Q_{atm} , that is absorbed by the pool and Q_{sur} , the long-wave radiation emitted at the surface of the pool. Both terms are calculated based on the Stefan-Boltzmann radiation law. The difference, $Q_{sur} - Q_{atm}$ is sometimes referred to as the effective back radiation, Q_{back} .

The energy emitted from the surface is:

$$Q_{sur} = \epsilon \sigma T_s^4 \quad (5)$$

where ϵ is the emissivity of the chemical,
 σ is the Stefan Boltzmann constant (2.04×10^{-7}) $\text{kJ/m}^2 \text{K}^4 \text{hr}$
 and T_s is the absolute surface temperature of the pool (K).

The emissivity term is required since the surface does not behave as a perfect black body. As before, the emissivity of the water surface, which has a value of 0.970 (Raphael, 1962), is used for the emissivity of the chemical since no emissivity data are available for most chemicals. This is supported by the fact that most natural surfaces have an emissivity of close to unity (Brutsaert, 1982).

The energy from the atmosphere by long-wave radiation is:

$$Q_{\text{atm}} = (1 - \eta) \beta \sigma T_a^4 \quad (6)$$

where η is the reflectivity of the surface with regard to long-wave atmospheric radiation, T_a is the absolute air temperature (K), and β is the atmospheric radiation factor.

Although the atmospheric radiation is a function of many variables, Anderson (1954) proposed an empirical relationship which correlates atmospheric radiation with air temperature, water vapour pressure, and cloud cover and height, which are, with the exception of cloud height, readily available or obtainable. A 10% accuracy was placed on this correlation. Raphael summarized and simplified Anderson's relationships and the results are shown in figure 3 which plots atmospheric radiation factor β as a function of cloud cover and vapour pressure of water in air without regard to cloud height. This enables the estimation of the radiation factor from conditions that are easily observed.

The product of β and σT_a^4 must be corrected for the reflection of atmospheric radiation. For a water surface, the reflectivity was found to be 0.03 (Raphael, 1962). Again, this value is recommended for clear, visually water-like chemicals.

3. Evaporation Energy

The energy required for evaporation is simply the product of the heat of vaporization and the rate of evaporation. That is,

$$Q_{\text{ev}} = E \Delta H_{\text{vap}} \quad (7)$$

where E is the evaporation rate ($\text{g/m}^2 \text{ hr}$) and ΔH_{vap} is the heat of evaporation (kJ/g). The evaporation rate may be determined from:

$$E = k M P(T_s) / RT_s \quad (8)$$

where k is the mass transfer coefficient (m/hr),

P is the vapour pressure of the chemical determined from the surface temperature T_s (Pa),

M is the molecular weight of the chemical,

and R is the gas constant ($8.314 \text{ Pa m}^3 / \text{mol K}$).

Therefore, combining equations (7) and (8):

$$Q_{\text{ev}} = k M P(T_s) \Delta H_{\text{vap}} / RT_s \quad (9)$$

This energy loss due to evaporation accounts for the phenomena known as the evaporative cooling effect.

4. Sensible Heat Exchange

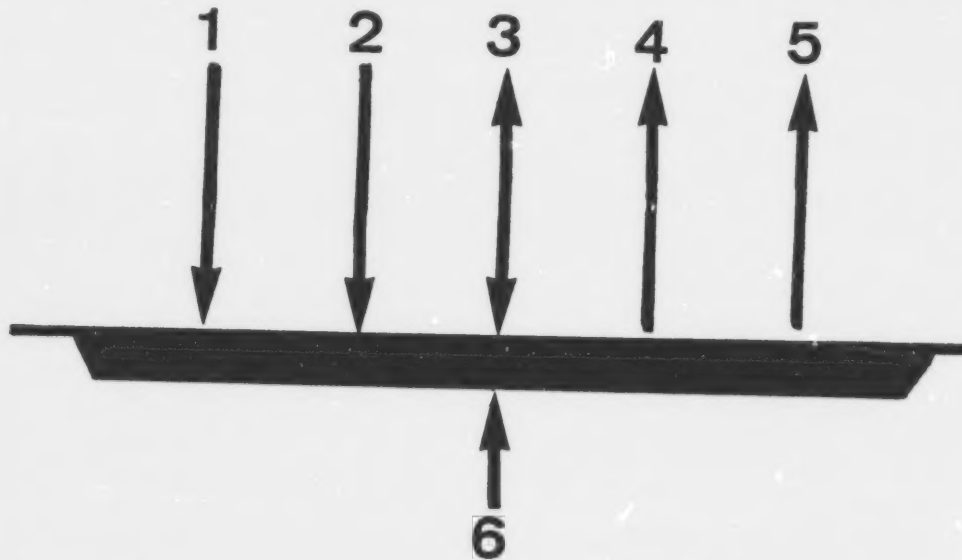
Sensible heat transfer occurs when there is a difference in temperature between the air and the surface of the pool. It may be written in the form:

$$Q_{sen} = U (T_s - T_a) \quad (10)$$

where U is the heat transfer coefficient ($\text{kJ/m}^2 \text{ hr } ^\circ\text{C}$), which is a function of wind speed, temperature, and other properties. T_a is the absolute temperature of the air.

5. Other Sources of Energy

This term may be employed to include other sources or sinks of energy that was not covered in the previous sections. One such example is the effect of heat conduction from the ground, which may be studied in the future.



- 1 NET SOLAR RADIATION**
- 2 ATMOSPHERIC RADIATION**
- 3 SENSIBLE HEAT**
- 4 EMITTED RADIATION**
- 5 EVAPORATION ENERGY**
- 6 GROUND CONDUCTION**

Figure 1: Steady State Energy Budget for an Evaporating Pool

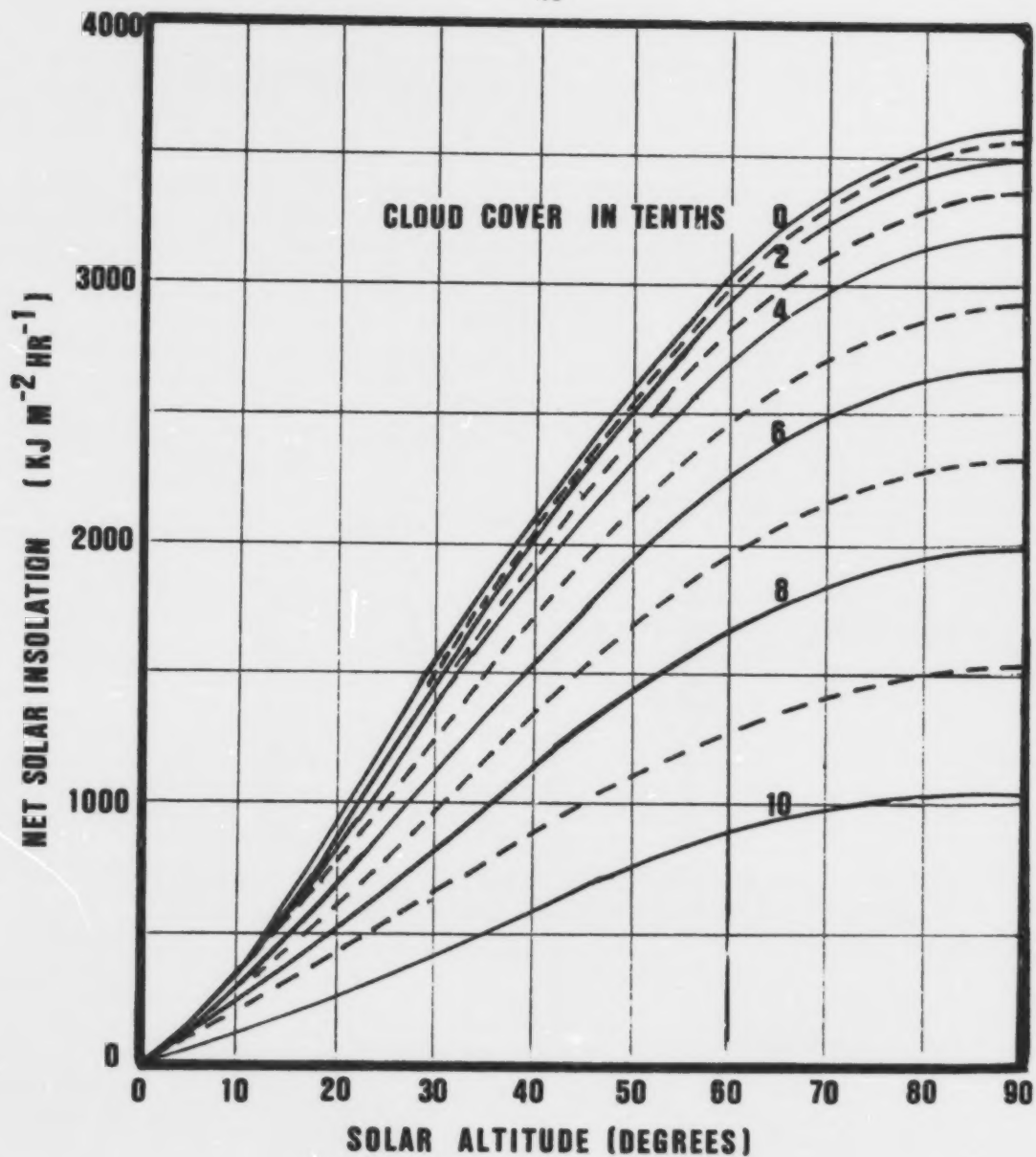


Figure 2: Effective Solar Insolation as a Function of Cloud Cover and Solar Altitude (Adapted from Raphael, 1962)

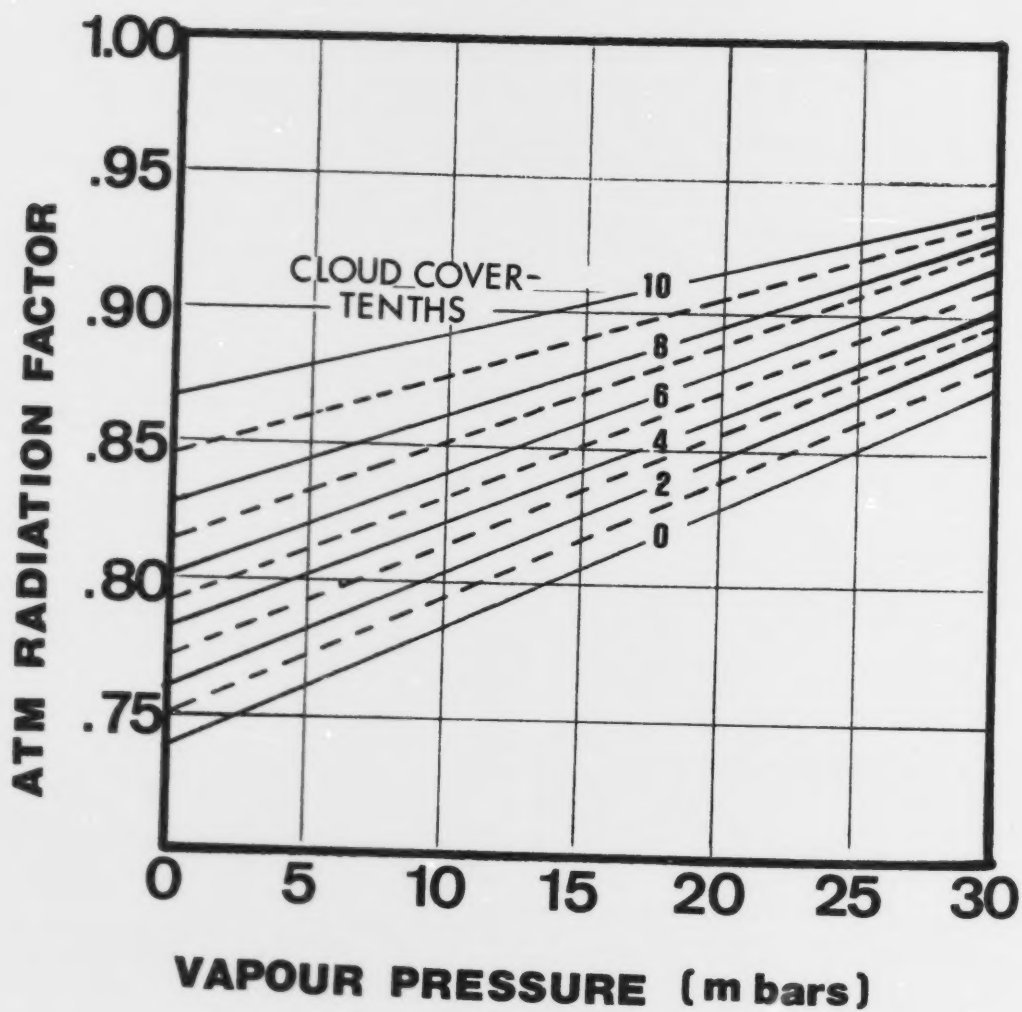


Figure 3: Atmospheric Radiation Factor as a Function of Cloud Cover and Water Vapour Pressure in the Atmosphere (Adapted from Raphael, 1962)

EVAPORATION MODELS

Two relatively simple evaporation models are presently being assembled to predict the steady state evaporation rate from ground spills. These are the direct evaporation method and the surface temperature method. Both models include the effect of solar radiation as well as evaporative cooling, and the mass transfer coefficient of Mackay and Matsugu (1973) is employed. This coefficient has the form

$$k = 0.0292 U^{0.78} X^{-0.11} Sc^{-0.67}$$

where k is the mass transfer coefficient, (m/hr)

U is the wind speed (m/hr)

X is the pool diameter or length (m)

and Sc is the chemical Schmidt number.

The required values for the models, such as solar radiation and long wave energy exchange terms are determined from equations and diagrams presented in the previous section. Effects of sorption and conduction of heat from the ground are neglected in both models. However, these effects may be added during a later stage of model development.

Direct Evaporation Method

This method is based on Penman's study of natural evaporation of water (1948). Few modifications have been made to adapt Penman's approach to the evaporation of a chemical under environmental conditions.

In studies relating to the evaporation of water, Bowen's ratio is frequently used. It is simply the ratio of the conduction of sensible heat to the energy lost by evaporation. The Bowen's ratio, Bo , is:

$$Bo = \gamma (T_s - T_a) / (P_s - P_a) \quad (12)$$

where γ is a constant,

P is the partial pressure of the substance at the surface (s), and in the air (a).

This ratio is a useful tool in the development of a model to predict the evaporation rate of a chemical based on energy balance but it cannot be utilized in this form, since it contains terms dependent on the surface temperature, which is unknown. The objective was to introduce certain expressions for these terms based on simplifying assumptions, existing theory, and correlations, which will result in an explicit relationship between the evaporation rate and terms which can be easily

determined. The development of this relationship is discussed in the following paragraphs.

The constant γ in the Bowen's ratio may be evaluated from equations 9 and 10 and from the heat and mass transfer analogy, which relates the heat and mass transfer coefficients by the following expression:

$$U = k \rho_a C_{pa} (Sc/Pr)^{0.67} \quad (13)$$

where ρ_a is the density of air (mol/m^3),
 C_{pa} is the heat capacity of air ($\text{kJ}/\text{mol K}$),
 Sc is the chemical Schmidt number
 Pr is the Prandtl number.

The density of air is simply the atmospheric pressure divided by the gas constant and the absolute temperature. Correcting for the molecular weight difference between the air and the chemical, the ratio γ is:

$$\gamma = 29 P_{atm} C_{pa} (Sc/Pr)^{0.67} / M \Delta H_{vap} \quad (14)$$

where P_{atm} is the atmospheric pressure (Pa), and the ratio has units of Pa/K.

To eliminate the surface temperature, T_s , which is unknown, the following assumption is made:

$$\Delta = (dP^*/dT)_{T_a} \approx [P(T_s) - P(T_a)] / (T_s - T_a) \quad (15)$$

where Δ is the slope of the vapour pressure curve for the chemical, and P^* is the saturated vapour pressure. The slope is approximated by evaluating the derivative of the vapour pressure equation at the air temperature. It should be noted that the term P_a in the Bowen's ratio is negligible, since the concentration of the chemical in the bulk air phase is essentially zero.

It is useful to define a term, Q , which can be viewed as the amount of chemical that can be evaporated by the energy exchange with the environment:

$$Q = (Q_{sol} + Q_{atm} - Q_{sur} + Q_{ext}) / \Delta H_{vap} \quad (16)$$

At this point, the ratios γ and Δ (identified by equations 14 and 15) are utilized in the steady state energy equation to yield the following expression for Q :

$$Q = [1 + (\gamma/\Delta)] E - [(\gamma/\Delta) (P(T_a)/P(T_s))] E \quad (17)$$

The term $P(T_s)$ can be eliminated by introducing equation 8 to the second term of the above equation. This yields:

$$Q = [1 + (\gamma/\Delta)] E - (\gamma/\Delta) E(T_a) \quad (18)$$

where $E(T_a)$ is the "evaporation rate", which is based on the air temperature to evaluate the vapour pressure. Note that $P(T_s)=P_s$; that is, the partial pressure of the chemical at the surface of the pool is equal to the saturated vapour pressure. $E(T_a)$ is thus,

$$E(T_a) = k P(T_a)/RT_a \quad (19)$$

Finally, equation 18 can be rearranged to give an explicit relationship for the predicted evaporation rate, E . This relationship is:

$$E = [\Delta/(\gamma + \Delta)] Q + [\gamma/(\gamma + \Delta)] E(T_a) \quad (20)$$

The advantages of using this equation to predict the evaporation rate are (i) it includes the effects of solar insolation and evaporation cooling; (ii) it eliminates the need to determine the pool or surface temperature; (iii) it is simple (no iteration or computer requirement); (iv) it is flexible and can include effects such as conduction from the ground, which can be absorbed into the term Q ; and (v) it is based on readily available physical-chemical data.

One drawback of this equation is that the long-wave radiation emitted by the surface of the pool, which is required for Q in equation 16 cannot be determined since this requires the knowledge of the surface temperature. However, this term is assumed to be approximately equal to the atmospheric radiation term for volatile chemicals under most conditions. Due to the temperature depression of the volatile chemical pool, Q_{sur} is expected to be less than Q_{atm} , based only on temperature considerations. But this "inequality" is, in part, compensated for by the atmospheric radiation factor which "suppress" this difference. Therefore, the back radiation, $Q_{back} = Q_{sur} - Q_{atm}$, is expected to be small compared to the solar insolation, except at periods close to sunrise or sunset and during night-time.

Based on this assumption, equation 16 may be reduced to:

$$Q = (Q_{sol} + Q_{ext}) / \Delta H_{vap} \quad (21)$$

This model is currently being tested against actual experimental data.

Surface Temperature Method

This method determines the surface temperature of the pool based on the steady state heat balance (equation 1 with $Q_t=0$). This temperature is then used to calculate the evaporation rate using equation 8.

The heat balance equation can be manipulated to yield the following:

$$0.97 \sigma T_s^4 + C k \Delta H_{\text{vap}} P(T_s) M/RT_s + U T_s = Q_{\text{sol}} + Q_{\text{ext}} + 0.97 \beta \sigma T_a^4 + U T_a \quad (22)$$

where C is a pressure conversion factor. Note that the left hand side of the above equation consists of terms which depend on the unknown surface temperature, whereas on the right hand side, the terms can be easily evaluated. (The value for U may be determined by equation 13.) If the right hand side of equation 22 is designated as a constant F , the equation becomes:

$$0.97 \sigma T_s^4 + C k \Delta H_{\text{vap}} P(T_s) M/RT_s + U T_s - F = 0 \quad (23)$$

where

$$F = Q_{\text{sol}} + Q_{\text{ext}} + 0.97 \beta \sigma T_a^4 + U T_a \quad (24)$$

Equation 23 may be solved for T_s by standard root determining methods such as Newton's, bisection, and globally convergent methods. This root, which is the surface temperature of the pool, is used to calculate the evaporation rate using equation 8. This procedure is best suited for a computer but the program required is very short and simple.

Of the methods available to solve equation 23, the Newton's method may be best suited for this problem since it is very simple and often converges to the desired root rapidly. For example, for an "accuracy" of 0.5 C in the surface temperature, which is a reasonable estimate, considering other uncertainties involved, only a few iterations is necessary, depending on the choice of the initial guess of T_s . This first estimate may be taken to be the air temperature for most chemicals but a guess of 10 to 20 C lower than the air temperature is recommended for very volatile chemicals. The latter recommendation may prevent oscillations about an imaginary root, which is possible, if the initial guess is not close to the actual surface temperature. This may not be a problem for other root-solving methods, but they require, in general, more programming and iterative steps.

Despite having to use a computer or a programmable calculator in this procedure, this method has the advantage of including all the energy exchange terms that are listed in the overall energy balance. If the assumptions made in the direct evaporation formula development are found to be invalid under certain conditions, this method should be implemented under these conditions. The general approach is thus to obtain experimental data, test the two models and select the better on the bases of accuracy and convenience.

EXPERIMENTAL

Experiments are currently being performed at the Environment Canada Atmospheric Environment Services site in Woodbridge, Ontario. The procedure involves evaporating a chemical from a circular stainless-steel pan under varying seasonal and atmospheric conditions. The size of the pans range from two to four feet in diameter, and the inner surface is painted black. The pan is insulated from the ground to prevent conduction of heat from the ground. The chemicals used in this study are toluene, xylene, pentane, cyclohexane, and methanol.

During the experiment, the evaporation rate, and the bulk pool and surface temperatures are measured. The latter is accomplished by using a thin thermocouple located at the surface of the pool. Atmospheric data, such as solar insolation, air temperature, wind speed, and cloud cover are also measured.

The data obtained are averaged over a defined time interval, such as one half or one hour, depending on the duration of the experiment. The experiment may last from one to four hours, during which time three to six litres of the chemical are evaporated. Experimental values of the air temperature, wind speed, and cloud cover are used as inputs to the two evaporation models, in which the predicted evaporation rate is compared to the actual evaporation rate. The other experimental data are used to calculate and compare the existing equations and correlations to the experimentally determined values. For example, the measured solar radiation is compared with Raphael's solar radiation curve (figure 2), and the mass transfer coefficient of Mackay and Matsugu is tested against the actual mass transfer coefficient calculated from measured surface temperatures.

CONCLUSIONS

Two models, the direct evaporation equation and the surface temperature method were developed, which we hope, will be able to predict the evaporation rate of pure liquid chemicals resulting from ground spills. These methods are relatively simple and based on available physical-chemical data. The main advantage of these models is that the effects of important variables, such as solar insolation and evaporative cooling are included. They are currently being tested and refined, based on results of outdoor experiments.

ACKNOWLEDGEMENTS

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ESTIMATING EXPOSURE FROM A CHEMICAL SPILLED INTO A RIVER

by

W. B. Neely¹ and R. W. Lutz²
The Dow Chemical Company

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¹Environmental Sciences Research, Midland, Michigan 48640

²Environmental Services, Fort Saskatchewan, Alberta, Canada

ABSTRACT

There is always the possibility of an accidental discharge of a chemical into a flowing river system. When it happens, knowledge is needed of the concentrations that can be expected downstream of the discharge. By taking advantage of an actual derailment in British Columbia it was possible to validate a set of dispersion equations for making such predictions. The model has been programmed to operate on a small microprocessor which makes the results immediately accessible to the decision makers.

INTRODUCTION

When an accidental discharge of a chemical occurs in a river there is an immediate need to know the risks associated with the exposure. For example, if municipalities downstream are using the river as a source of drinking water then it becomes necessary to make a decision regarding closing the water intakes. These and other types of questions can be answered more intelligently if information is quickly available on both effects and exposure. The purpose of the present report is to update our previous work on the exposure side of this question (1-3). The effects will be the subject of a future article.

The basis for the model used in predicting concentrations will be presented along with a report on an actual accident. The results from the theoretical analysis will then be compared to the measured values.

MODEL DESCRIPTION

The mathematical description of how a material disperses in a river has been investigated by many authors (4,5). For a detailed derivation of the equations either of these two references should be examined. The present discussion will be limited to a general overview.

Once a material has been added to a flowing water system it begins to spread in all three directions where the dispersion is controlled by the coefficients D_x , D_y and D_z . In the case of a river the vertical mixing

in the z direction is relatively fast compared to the lateral (y) and longitudinal (x) mixing, and to a first approximation may be ignored. Accordingly, the concentrations at any point downstream from the spill is given by equation 1

$$C(x,y,t) = C_1(x,t) C_2(y,t) \quad (1)$$

where $C(x,y,t)$ is a product of two one dimensional equations.

$$C_1(x,t) = \frac{M}{(4 \pi D_x t)^{0.5}} \exp\left(-\frac{x^2}{4D_x t}\right) \quad (2)$$

where M = amount spilled

D_x = diffusion coefficient

and a similar equation for $C_2(y,t)$ (4).

Multiplying C_1 by C_2 yields 3.

$$C(x,y,t) = \frac{M}{4 \pi t(D_x D_y)^{0.5}} \exp\left(-\frac{x^2}{4 D_x t} - \frac{y^2}{4 D_y t}\right) \quad (3)$$

By including advection in the direction of stream flow the final diffusion equation in two dimensions is derived.

$$C(x,y,t) = \frac{M}{4 \pi t(D_x D_y)^{0.5}} \exp\left(-\frac{(x-vt)^2}{4 D_x t} - \frac{y^2}{4 D_y t}\right) \quad (4)$$

where v = velocity of stream flow

Since only maximum concentrations are of concern the exponential terms in equation 4 will be equal to 1. Thus the maximum concentration at any point downstream along the center line of the spill ($y=0$) is given by 5.

$$C(x,t) = \frac{M}{4 \pi t (D_x D_y)^{0.5}} \quad (5)$$

If the discharge of material occurs near the bank of the river, the estimated concentration in equation 5 needs to be multiplied by 2. The factor 2 is derived from the observation that material added in the middle of the river may disperse towards each bank. This should be compared to the situation for a spill from the side where the lateral dispersion occurs in only one direction.

As soon as the material becomes uniformly distributed across the width of the river the concentration is given by equation 6.

$$C(x,t) = M/[A (4 \pi D_x t)^{0.5}] \quad (6)$$

where A = cross-sectional area of the river

The distance required for uniform mixing is a function of the width, shear velocity and dispersion coefficient in the lateral direction (4,6). If the chemical is discharged in the middle of the river the mixing length is determined by equation 7.

$$L = (0.1 U^* W^2) / D_y \quad (7)$$

where U^* = shear velocity

L = length in meters from the spill site

On the other hand, if a material is spilled from the shore, as in a derailment, the length required is four times the distance indicated in equation 3 (6). Both of these estimations apply to a straight channel. If there are many bends in the river, consideration should be given to modifying this length. The above discussion has assumed that the chemical is conservative, i.e., there are no dissipating reactions operating. It is generally accepted that loss mechanisms operate via a first order process, consequently each of the concentration equations should be multiplied by equation 8 where Σk represents the sum of all

$$\exp(\Sigma kt) \quad (8)$$

the rate constants responsible for removing the chemical from the water system.

Estimating the Hydrodynamic Constants

From equations 5 and 6 it is apparent that the key properties required for an analysis are M , the amount of chemical added to in the water column, the shear velocity, and the two dispersion coefficients, D_x and D_y . If available these values should be based on the actual conditions of the spill site. In the absence of field data the following procedures will generate the three hydrodynamic coefficients.

a. Shear Velocity -- To a first approximation the shear velocity is about 0.1 times the mean velocity of the river (4).

b. Longitudinal Dispersion Coefficient -- This becomes a very critical coefficient since the extent of spreading in the direction of flow is directly related to the magnitude of this number. There have been many studies on how to estimate D_x using readily available river data. After examining the many correlations the one that has the most acceptance is the analysis by Liu (7,8) summarized in equation 9.

$$D_x = 0.5 U^* W^2/d \quad (9)$$

where W = width

U^* = shear velocity

d = depth

c. Lateral Dispersion Coefficient -- Fisher et al. (4) have reviewed the present state of knowledge for estimating D_y . This is illustrated with equation 6, where the value of A varies with the type of stream.

$$D_y = A d U^* \quad (10)$$

For straight channels A is in the range of 0.1 to 0.2. Irregularities cause the coefficient to increase. For most streams, including the present analysis, A is given a value of 0.6.

THE ACCIDENT

At 1527 hours (3:27PM) Pacific time on March 3, 1982, a train operated by the Canadian National Railway was derailed 8 miles south of Blue River, British Columbia. The accident allowed 1.74 million pounds of ethylene dichloride (EDC) to enter the Thompson River. An emergency response team from Dow Canada located at Fort Saskatchewan, Alberta was alerted and immediately flown to the scene. Through their efforts a great deal of monitoring data was obtained which will form the basis for validating the proposed model. The field data is shown in Tables I and II. Table I also includes several relevant observations that were made regarding the topography of the spill site.

Table III contains the available hydrological information on the Thompson River as well as the climatic conditions at the time of the accident. Table IV summarizes the key properties of ethylene dichloride.

RESULTS

Several simulations will illustrate how estimations can be improved by including more site specific data. Improvement will be judged by how close the predictions are to the measured concentrations as shown in Table I. The results are reported in Table V as concentrations of EDC, 28 and 60 miles downstream of the accident. The simulations will progress from a minimum data base to the situation where all the available information is used.

a. Simulation 1 -- Incorporating the hydrological data in Table III into the model equations, a spill of 1.74 million pounds (7.88×10^5 kilograms) of EDC was simulated. For this first case EDC was treated as a conservative chemical. This is a worst case situation which will yield the maximum predicted concentrations. As can be seen from Table V this is exactly what occurred. With the inclusion of more site specific data the results should begin to approach the measured values.

b. Simulation 2 -- There are two possible mechanisms for dissipation of EDC from the river. These are adsorption to sediments and volatility. With the low value for the partition coefficient (Table IV) it would be predicted that binding of EDC to sediments would be small. This is partially substantiated by the work of Dilling *et. al.* (9). While these authors did not investigate EDC, they did study chloroform a halocarbon with very similar properties. In their report (9) the conclusion was reached that little or no binding of CHCl_3 to sediments occurred. Accordingly, adsorption will be ignored as a possible mechanism for lowering the water concentration of EDC.

In order to evaluate the rate constant for volatility it is necessary to have a vapor pressure at the temperature of interest (4°C). The procedure described by Grain (11) was used for this estimation. By applying the model of Liss and Slater (12) as modified by Wolff and van der Heijde (13) the loss by volatility under the influence of a 4 m/s wind speed was calculated (Table IV). Since the river was 50% covered with ice, the rate constant had to be reduced by one-half before using it in equation 4. The results of including volatility are shown in Table V.

c. Simulation 3 -- The concentration numbers in Table V from the previous simulation are still too large which would suggest that either the initial input was too great or some other loss mechanism must be operating. Since the major route of dissipation was considered in Simulation 2, the present Simulation will focus on the actual amount of chemical that entered the river.

Ethylene dichloride is slightly soluble and heavier than water, consequently the bulk of the material will fall to the bottom of the water column as a cohesive mass. Once on the bottom the material can form pools. Some of these pools may be protected from the turbulent action of the river and will form a reservoir which will be slowly solubilized. The problem of estimating how much of the discharge is solubilized has been studied by Thibodeaux (14) and was discussed by Neely et al (1).

At this time only a crude calculation of the initial amount in solution will be made based on the study of the chloroform accident (1). From that analysis it was estimated that about 15-20% of the original mass went into solution. The remainder was on the bottom and contributed to the residual tail that was observed long after the initial wave front had passed (1). By accepting the hypothesis that miscible materials go into solution quickly as compared with 20% for chemicals like chloroform Table VI was formulated. Recognizing that the fractions assigned are arbitrary, it appears to be a reasonable first approximation of what will occur during a spill. Obviously, this is an area that needs further study.

Since the solubility of chloroform (10,000 mg/L) (9) is similar to EDC (Table IV), it will be assumed that 20% of the 1.74 million pounds (1.57×10^5 kilograms) of EDC is immediately solubilized. The remainder goes into solution over a period of several days giving rise to the low background level of EDC reported in Table II. The results of this simulation are shown in Table V.

In most cases the simulations would stop at this point since it is most unlikely that additional information would be available. The next step would be to make predictions of concentrations with distance and match these values with the toxicological information.

d. Simulation 4 -- From Table V it is seen that the data at mile 28 are close to the measured values. The major discrepancy is at mile 60 where the concentration is too high and the time of arrival is too long. From Fisher et al. (4) the length of river necessary to contain 95% of the mass is given by equation 7.

$$L = 4(2 D_x t)^{0.5} \quad (7)$$

From equations 4 and 5, D_x is estimated to be $31.6 \text{ m}^2/\text{s}$. Using equation 7, L at 68 hours becomes 16 km. However the actual data in Table I indicates that 32 miles or 51 km is a more appropriate value. Substituting this new value for L into equation 7, D_x is calculated to be $334 \text{ m}^2/\text{s}$ at 68 hours. By noting the time of arrival of the peak at mile 60, a velocity of 0.39 m/s was estimated. Using these two numbers simulation 4 was carried out with the results indicated in Table 5. As

can be seen the new predictions at mile 60 are in close agreement with the measured numbers. The revised estimates of the dispersion coefficient and velocity are a direct consequence of the rapids between mile 32 and 48 (Table 1). This is a further illustration of how site specific information can improve the predictions.

e. Simulation 5 -- This simulation was performed to demonstrate the influence of climatic conditions. Everything was similar to number 3 except that the water temperature was increased to 20°C. In effect this will approach summer conditions. From the results in Table V it is obvious that the change in temperature causes a more rapid loss of EDC (half-life of 41 hours under summer conditions compared to the 57 hours for simulation 3).

CONCLUSION

Given the hydrological data on a river it is apparent that reasonable estimations of the concentrations downstream from a spill site can be derived. Furthermore, the more site specific information that is available the closer the predictions will be to the measured numbers. In the final analysis if the analyst had all the data there would be a theoretical one to one correspondence between prediction and observation. Recognizing that the ideal is never reached it is still necessary to approach the goal as closely as possible. From an emergency response point of view the initial predictions are ideal in that they are conservative. Thus, with minimum data the concentration numbers are high and

the risk assessment will be on the safe side. It is only by including more site specific information that the predictions can be lowered.

The equations and data have been programmed to run on the IBM Personal Computer. Such a system makes for rapid analysis which is exactly what is needed during an emergency. Consequently, as new information is made available the predictions can be quickly updated for the benefit of the decision makers at the scene of the accident.

TABLE I. Field Data from the Site of the Accident

Distance (miles)	Time Post Derailment (hours)				Site Conditions
	44	68	92	20 hours ^a	
.1				no	opposite from spill
.1	8 ^b	6	10	yes	same side
4	4				
5				yes	both sides of
5				yes	the river
7				yes	mile 1 to 10
8	5	7	4		rapids
10				yes	
12	14				mile 16 to 32
16	45			no	is flat
20	80				and
21				no	ice covered
28	220	12	15		
32	180				mile 32 to 48
40	N.D.		10		rapids
52	N.D.	33	18		
60		40			mile 52 to 100
64			13		generally flat
68		19			and wide
72			8		
80		12	14		

^aThis column refers to the detection of odor.

^bConcentrations are in mg/L.

TABLE II. Concentration of Ethylene Dichloride in the Thompson River

<u>Days^a After Accident</u>	<u>From the Site Concentration in mg/L</u>		
	<u>0.01 km</u>	<u>38 km</u>	<u>51 km</u>
6		3.9	3
7	22		
8	7	3	2
9	3.6	2	1.7
14	3.2	N.D.	N.D.

^aDerailment occurred on March 3, 1982.

TABLE III. Hydrological and Climatic Conditions at the Time of the Accident

Flow	25.2 m ³ /s
Depth	1.5 meters
Velocity	0.3 meters/s
Water Temperature	4°C
Air Temperature	10°C
Wind Speed	4 m/s
Surface of water 50% covered with ice	

TABLE IV. Chemical and Physical Properties of Ethylene Dichloride

Molecular Weight	98.9
Melting Point	-35°C
Boiling Point	83.3°C
Water Solubility (20°C)	8800 mg/L
Vapor Pressure (25°C)	0.11 atmospheres
Flash Point	18°C
Specific Gravity	1.2457
Octanol Water Partition Coefficient	250

Estimated Properties

Vapor Pressure (4°C)	0.03 atmospheres
Rate Constant for Volatility at 4°C and Wind Speed of 4 m/s	1.16×10^{-2} m/hr

TABLE V. Results of Simulation Studies Compared to Measured Values

	Concentration of EDC (mg/L) at	
	<u>28 Miles</u>	<u>60 Miles</u>
Measured Values	220(44) ^a	40(68)
Simulations		
1. Conservative	1211(42)	827(89)
2. Volatility	1030(42)	584(89)
3. Reduced Input	207(42)	117(89)
4. Velocity = 0.39 D _x = 334 m ² /s		58(68)
5. Summer Conditions Water Temperature 20°C	171(42)	78(89)

^aNumber in parenthesis indicates time in hours after the accident where the concentration was either measured or predicted.

TABLE VI. Solubility vs. Fraction of Material That Goes Into Solution

<u>Class</u>	<u>Solubility (mg/L)</u>	<u>Fraction Solubilized</u>
Insoluble	<1,000	0.05
Slightly Soluble	1,000-50,000	0.20
Moderately Soluble	50,000-500,000	0.5
Very Soluble	500,000-1,000,000	0.8
Miscible	>1,000,000	1.0

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ESTIMATION OF PHYSICAL AND CHEMICAL PROPERTIES

P.T. Chung
Underdown Chemometrics Limited
Nepean, Ontario

INTRODUCTION

A systematic assessment of risk associated with the production, transportation and use of chemicals requires information on both toxicological and physicochemical properties. Basic physical and chemical data, necessary for accurate environmental modelling, are often lacking. This paper describes a portion of our recent work on the data management and evaluation of the physical and chemical properties of frequently spilled hazardous materials.

The objective of this paper is to test the validity of several estimation methods over a wide range of environmental conditions (such as temperature and pressure) and for a representative selection of chemical compound types. The estimation equations used for the prediction of normal boiling point, liquid specific gravity, vapour pressure, vapour density, and flash point are discussed. Sample calculations are presented for a series of polychlorinated biphenyls (PCB's), and the results compared to the measured values for commercially formulated PCB mixtures as reported in the "Manual for Spills of Hazardous Materials" (TSB 1984). Estimated and measured values for the list of selected chemicals (see Table 1) are presented, and the accuracy of the prediction equations are discussed.

BOILING POINT ESTIMATION

The normal boiling point of a chemical compound is the temperature at which the saturated vapour pressure of the chemical is at one atmosphere (101.3 kPa). Boiling point determinations indicate that physical state in which the chemical exists under specific environmental conditions and also provide some measure and indication of the volatility of the chemical. In addition, it can be used to predict many physical properties of the chemical (OECD 1981, Lyman 1982, TSB 1984).

Many methods are available to estimate the normal boiling point of simple chemical compounds. The general approach assumes that the effects of attaching multiple substituent groups to a molecule are additive and independent of each other (Lyman 1982):

- a) The method of Stiel and Thodos is applicable to normal alkanes:

$$t_b = 936 - \frac{1163}{1 + 0.074 (N^{0.85})} \quad (1)$$

where: t_b is normal boiling point ($^{\circ}\text{C}$)
N is number of carbons in the compound

- b) Ogata and Tsuchida developed an estimation equation for the normal boiling point of chemicals of the form R-X, where R is a hydrocarbon radical and X is a functional group. The estimation method is restricted to compounds containing one functional group, such as -Cl, -Br, -OH, -SH, -NH₂, -COH and -COOH. The selection of hydrocarbon radical groups is limited to a small group of hydrocarbons with less than 7 carbon atoms (excluding fused ring hydrocarbons). The boiling point is estimated as follows:

$$t_b = p(y) + q - 273 \quad (2)$$

where: y is related to the hydrocarbon radical group (R)
p & q are characteristic constants for the functional group (X)

- c) Somayajulu and Palit developed a three parameter correlation for normal hydrocarbons containing one functional group. This method is applicable to the following: n-alkyl halides; n-alkyl aldehydes; n-alkyl ketones; n-alkyl acids; n-alkyl ethers; n-alkyl acetates; n-alkyl amines; n-alkyl benzenes; n-alkyl cyclohexanes; n-alkanes; n-alkenes; n-alcohols and n-alkanethiols. The equation is:

$$t_b = r(\text{sum of } Z's)^t + s - 273 \quad (3)$$

where: r, t & s are parameters dependent upon the homologous hydrocarbon series

(sum of Z's) is the sum of the atomic numbers of the atoms in the compound

- d) Kinney's method correlates normal boiling points with a boiling point number (Y). It is applicable to alkanes, alkenes, alkynes, cycloalkanes, and cycloalkenes. The equation, which is not applicable to halide-containing compounds, is:

$$t_b = 230.1(Y^{0.333}) - 543 \quad (4)$$

The boiling point number of a compound can be obtained from adding the individual boiling point numbers of the atoms and chemical bonds.

- e) The Meissner's method correlates normal boiling points with molar refraction (R_d), parachor (P), and an empirical constant B. This is applicable to organic compounds containing C, H, N, O, S, and halides:

$$t_b = \frac{637(R_d^{1.47}) + B}{P} - 273 \quad (5)$$

The molar refraction can be estimated by adding the individual atomic contributions from a table, or calculated more accurately if the refractive index at the sodium D line and the liquid density are available. The parachor can be estimated by the McGowan's or the Sugden's methods or calculated if the surface tension, vapour and liquid densities are known. The constant B is tabulated according to functional group.

The boiling points of PCB's are estimated using the Meissner's method as it is the only method applicable to chlorinated compounds with more than one functional group. Detailed calculations for three pure PCB's along with the measured value for a commercial formulation are shown in Table 2. The estimated boiling points are slightly lower than the measured value. The estimated boiling points for the group of representative chemicals are plotted against the measured boiling points from the "Manual" (TSB 1984) in Figure 1. The slope and intercept of the best linear fit through the data points indicates good correlation between the measured and estimated boiling points. Large deviations were observed for highly chlorinated alkanes, bi-functional alkenes and cyclic ethers.

LIQUID SPECIFIC GRAVITY ESTIMATION

The specific gravity of a liquid is the ratio of the weight of a given volume of a liquid at a specified temperature to the weight of an equal volume of water at a specified temperature. A test temperature of 20°C is used for most chemicals, and when a water temperature of 4°C is used, the density and specific gravity is numerically equal. In environmental analysis, the specific gravity of a chemical is used to determine its flotability in water (OECD 1981, Lyman 1982).

Grain's method is a simplification of the Goldhammer's method, where the molar volume at the normal boiling point and the critical temperature are estimated. The effect of pressure on liquid specific gravity is small and is neglected. The equation is (Lyman 1982):

$$SG = \frac{M}{V_b D} [3 - 2(T/T_b)]^n \quad (6)$$

where: SG is specific gravity

M is molecular weight (g/g-mole)

V_b is molar volume at normal boiling point (ml/g-mole)

D is density of water at a standard temperature (g/ml)

T is temperature (K)

T_b is normal boiling point (K)

n is a constant dependent on the chemical types.

The molar volume at the normal boiling point is estimated by adding the incremental values for every atom, chemical structure, and bond of the chemical.

The estimated and experimental specific gravity of PCB's are compared in Table 3. The estimated specific gravity is just within the specific gravity range of the commercially available PCB's indicating fair agreement between the estimated and measured values. The estimated specific gravity of the selected chemicals is plotted against the measured values from the "Manual" (TSB 1984) in Figure 2. The slope and intercept of the best linear fit through the data indicates good correlation between measured and estimated values. The estimated specific gravity of formaldehyde has a large deviation from the measured value. However, a review of the literature (Kirk-Othmer 1980) indicates that the measured value in the Manual is not accurate.

LIQUID VAPOUR PRESSURE ESTIMATION

The vapour pressure of a chemical is defined as its equilibrium partial pressure in a closed container containing the chemical and air at a specified temperature and pressure. Vapour pressure is a good indicator for the volatility of the chemical. Vapour pressure data combined with water solubility data permits the calculation of Henry's law constant, which is essential to estimate the evaporation rate of the chemical in a solution (OECD 1981, EPS 1982).

Starting from the Clausius-Clapeyron equation, Grain's method applied the modified Watson correlation to approximate the heat of vaporization at the normal boiling point to obtain the following vapour pressure estimation equation (Lyman 1982):

$$\ln VP = \frac{H}{Z R T_b} \left[1 - \frac{(3-2T/T_b)^m}{T/T_b} - 2m(3-2T/T_b)^{m-1} \ln (T/T_b) \right] \quad (7)$$

where: VP is vapour pressure (atm)

H is heat of vaporization at normal boiling point (cal/mol)

Z is compressibility factor at normal boiling point

R is gas constant (1.987 cal/mol K)

T_b is normal boiling point (K)

T is temperature (K)

m is exponent in the Watson correlation

The compressibility factor is assumed to be 0.97 at most environmental conditions. The exponent m has a value of 0.19 for all liquids. The heat of vaporization is estimated as follows:

$$\frac{H}{T_b} = Kf(8.75 + R \ln T_b) \quad (8)$$

where: Kf is derived from the molecular dipols moments and is available in tabulated form.

The measured and estimated vapour pressure for PCB's are shown in Table 4. The estimated vapour pressure of a series of pure PCB's is much lower than the measured vapour pressure of a commercial PCB mixture. Estimated vapour pressure of selected chemicals are plotted against measured vapour pressure in Figure 3. The slope and intercept of the best linear fit indicates good correlation between the measured and estimated values.

VAPOUR DENSITY ESTIMATION

The density of a chemical vapour is the ratio of its weight to the weight of an equal volume of dry air at the same pressure and temperature. It is a function of molecular weight and structure. Vapour density determines whether the vapour of a chemical will rise or sink, and thus its dispersibility, in air (Lyman 1982, TSB 1984, ASTM D 1070).

Under most environmental conditions, the ideal gas law is a good estimate of the vapour density of a chemical (Lyman 1982):

$$\text{Vapour Density} = \frac{\text{Molecular Weight of Chemical}}{\text{Molecular Weight of Air}} \quad (9)$$

Vapour densities of PCB's were not available in the "Manual" (TSB 1984). Estimated vapour densities of the selected chemicals are plotted against the measured values from the Manual in Figure 4. Good agreement is obtained between the measured and estimated values.

FLASH POINT ESTIMATION

Flash point is defined as the lowest temperature, corrected to one atmosphere (101.3 kPa), at which a chemical emits sufficient vapour above its surface that the application of an ignition source causes the vapour to ignite under the specified test conditions. Flash point is used to determine the relative flammability of chemicals (Lyman 1982, TSB 1984, Lance 1979).

The following correlation was observed by Butler, and subsequently improved by Hagopian (Lyman 1982):

$$FP = a (t_b) - b \quad (10)$$

where: FP is flashpoint (°C)

t_b is boiling point (°C)

a & b are constants depending on the chemical type

The constants a and b for several classes of chemicals, and the applicable range of the equation, are tabulated in Table 5.

The measured and estimated closed cup flash points of PCB's are shown in Table 6. The estimated flash points of the pure PCB's are in the range of the measured value. The estimated flash point of the selected chemicals are plotted against the measured values from the "Manual" (TSB 1984) in Figure 5. The slope and intercept of the best linear fit through the data points indicates good agreement between the measured and estimated flash points. The deviation between the estimated and measured flash points are higher for chlorinated alkanes, and for chemicals where specific estimation equations for the class of chemicals are not available (i.e. when the general hydrocarbon equation is used).

CONCLUSION

The estimation methods provided reasonably good results for "simple" chemical compounds. They are recommended for more "complicated" compounds only if a high degree of accuracy of the results is not required.

TABLE 1

LIST OF SELECTED CHEMICALS FROM THE MANUAL FOR
SPILLS OF HAZARDOUS MATERIALS (TSB 1984)

<u>CHEMICAL GROUP AND CHEMICAL</u>	<u>CHEMICAL FORMULA</u>
a) Alkanes	
methane	CH ₄
propane	n-C ₃ H ₈
butane	n-C ₄ H ₁₀
hexane	n-C ₆ H ₁₄
methyl chloride	CH ₃ Cl
methylene chloride	CH ₂ Cl ₂
chloroform	CH Cl ₃
carbon tetrachloride	C Cl ₄
ethyl chloride	CH ₃ CH ₂ Cl
1,1,1-trichloroethane	CH ₃ C Cl ₃
b) Alkenes	
ethylene	CH ₂ =CH ₂
propylene	CH ₃ CH=CH ₂
butylene	CH ₃ CH ₂ CH=CH ₂
vinyl chloride	CH ₂ =CH Cl
perchloroethylene	Cl ₂ C=C Cl ₂
methyl acrylate	CH ₂ =CHCOOCH ₃
ethyl acrylate	CH ₂ =CHCOOCH ₂ CH ₃
c) Alkynes	
acetylene	HC CH
d) Hydroxyls	
methanol	CH ₃ OH
ethyl alcohol	CH ₃ CH ₂ OH
n-butyl alcohol	CH ₃ CH ₂ CH ₂ CH ₂ OH
isopropyl alcohol	CH ₃ CH (OH) CH ₃
sec-butyl alcohol	CH ₃ CH (OH) CH ₂ CH ₃
ethylene glycol	HO CH ₂ CH ₂ OH
1,3-propylene glycol	HO CH ₂ CH ₂ CH ₂ OH

TABLE 1 (con't)

LIST OF SELECTED CHEMICALS FROM THE MANUAL FOR
SPILLS OF HAZARDOUS MATERIALS (TSB 1984)

<u>CHEMICAL GROUP AND CHEMICAL</u>	<u>CHEMICAL FORMULA</u>
e) Ethers	
dimethyl ether	$\text{CH}_3 \text{ O } \text{CH}_3$
ethylene oxide	cyclic $(\text{CH}_2 \text{ O } \text{CH}_2)$
propylene oxide	cyclic $(\text{CH}_2 \text{ O } \text{CH}) -\text{CH}_3$
f) Aldehydes	
formaldehyde	$\text{H}_2\text{C}=\text{O}$
acetaldehyde	$\text{CH}_3\text{CH} (= \text{O})$
butyraldehyde	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} (= \text{O})$
g) Ketones	
acetone	$\text{CH}_3\text{C} (= \text{O}) \text{CH}_3$
methyl ethyl ketone	$\text{CH}_3\text{C} (= \text{O}) \text{CH}_2\text{CH}_3$
h) Carboxylic Acid	
formic acid	HCOOH
acetic acid	CH_3COOH
stearic acid	$\text{CH}_3 (\text{CH}_2)_{16} \text{COOH}$
i) Esters	
ethyl acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$
amyl acetate	$\text{CH}_3\text{COO} (\text{CH}_2)_4 \text{CH}_3$
j) Anhydrides	
acetic anhydride	$\text{CH}_3\text{COOCOCH}_3$
k) Benzenes	
benzene	C_6H_6
toluene	$(\text{C}_6\text{H}_5) \text{CH}_3$
ethylbenzene	$(\text{C}_6\text{H}_5) \text{CH}_2\text{CH}_3$
l) Cyclic Compounds	
cyclohexane	C_6H_{12}

TABLE 2

MEASURED AND ESTIMATED BOILING POINT: PCB's

<u>CHEMICAL</u>	<u>Rd</u>	<u>P</u>	<u>B</u>	<u>t_b</u> (°C)
Measured Values:				
PCB mixtures				360 to 390 (TSB 1984)
Estimated Values:				
C ₁₂ H ₇ Cl ₃	65.015	498.8	7000	332.7
C ₁₂ H ₆ Cl ₄	69.882	538.4	11700	355.9
C ₁₂ H ₅ Cl ₅	74.749	578	15000	379.6

TABLE 3

MEASURED AND ESTIMATED LIQUID SPECIFIC GRAVITY: PCB's, 20°C

<u>CHEMICAL</u>	<u>M</u> (g/mole)	<u>V_b</u> (ml/mole)	<u>n</u>	<u>Specific Gravity</u>
Measured Values:				
PCB mixtures				1.3 to 1.5 (TSB 1984)
Estimated Values:				
C ₁₂ H ₇ Cl ₃	257.54	234.5	0.31	1.37
C ₁₂ H ₆ Cl ₄	291.98	252	0.31	1.45
C ₁₂ H ₅ Cl ₅	326.42	269.5	0.31	1.53

TABLE 4

MEASURED AND ESTIMATED LIQUID VAPOUR PRESSURE: PCB's, 25°C

<u>CHEMICAL</u>	<u>Kf</u>	<u>H/Tb</u>	<u>m</u>	<u>vp</u>
		(cal/mole K)		(mm Hg)
Measured Values:				
PCB mixtures				0.006 (TSB 1984)
Estimated Values:				
C ₁₂ H ₇ Cl ₃	1.01	21.69	0.19	0.0015
C ₁₂ H ₆ Cl ₄	1.01	21.77	0.19	0.0005
C ₁₂ H ₅ Cl ₅	1.01	21.84	0.19	0.0002

TABLE 5

THE CONSTANTS a AND b FOR FLASH POINT ESTIMATION EQUATIONS (Lyman 1982)

<u>CHEMICAL GROUP</u>	<u>a</u>	<u>b</u>	<u>Applicable Range</u>
All Hydrocarbons			
closed cup	0.683	71.7	66 to 288
open cup	0.683	67.4 *	66 to 288
Normal Alkanes	0.6946	73.7	C ₁ to C ₁₄
Alcohols			
closed cup	0.7056	48.1	82 to 255
open cup	0.6875	42.4	82 to 263
Aldehydes			
closed cup	0.6901	56.8	21 to 165
open cup	0.7491	64.3	21 to 243
Amines			
closed cup	0.7962	70.8	49 to 277
open cup	0.7988	67.0	32 to 278
Ketones			
closed cup	0.6717	58.7	56 to 223
open cup	0.6917	55.3	56 to 218

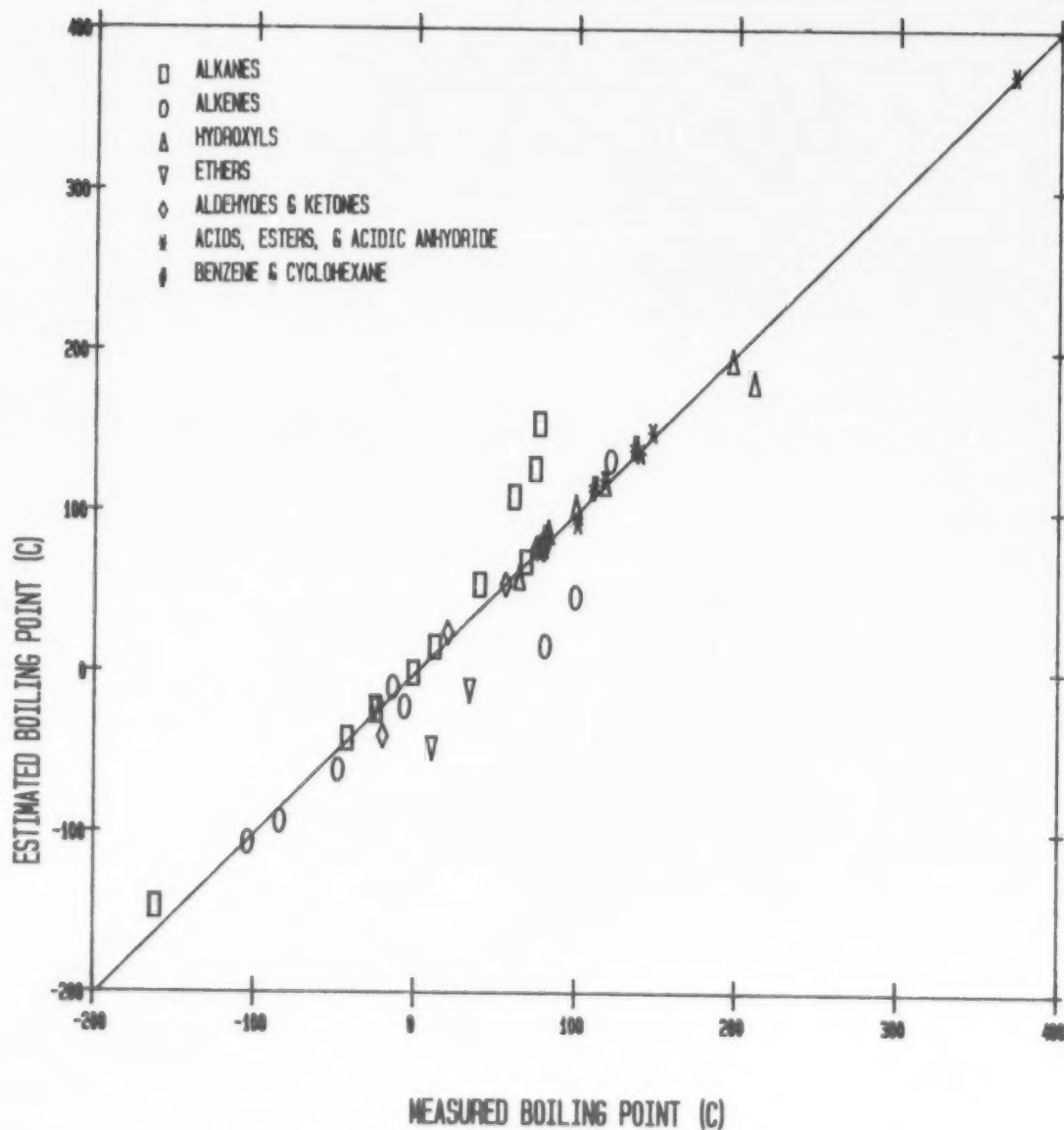
* Estimated value

TABLE 6

MEASURED AND ESTIMATED CLOSED CUP FLASH POINT: PCB's

<u>CHEMICAL</u>	<u>a</u>	<u>b</u>	<u>Flash Point</u> (°C)
Measured Values:			
PCB mixtures			>140 (TSB 1984)
Estimated Values:			
C ₁₂ H ₇ Cl ₃	0.683	71.7	155.5
C ₁₂ H ₆ Cl ₄	0.683	71.7	171.4
C ₁₂ H ₅ Cl ₅	0.683	71.7	187.6

FIGURE 1. BOILING POINT ESTIMATION



NOTES:

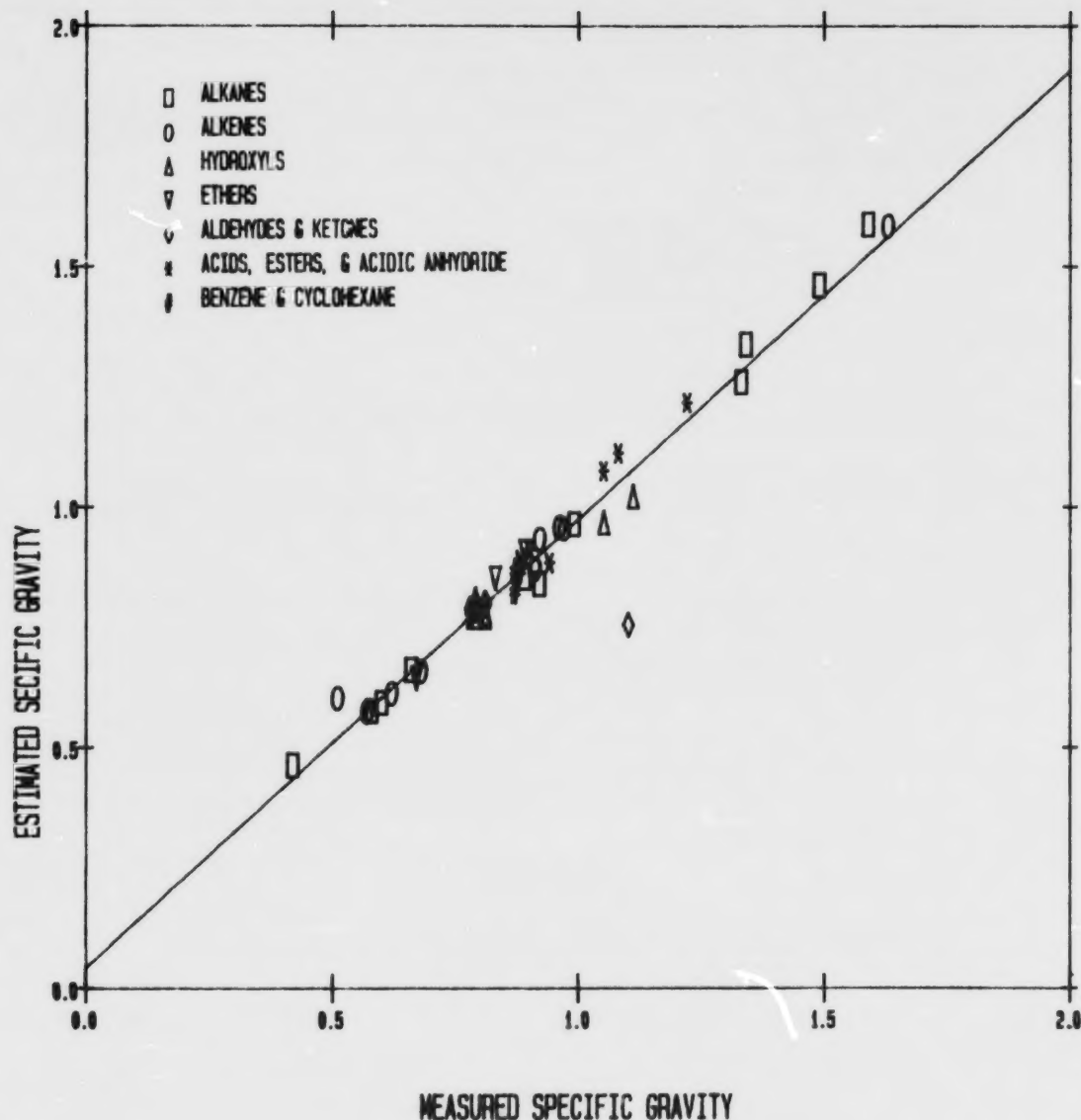
SLOPE OF BEST FIT LINE IS 1.0

INTERCEPT OF BEST FIT LINE IS -2.3

AVERAGE ERROR IS 2.1 C

AVERAGE % ABSOLUTE ERROR IS 4.5%

FIGURE 2. SPECIFIC GRAVITY ESTIMATION



NOTES:

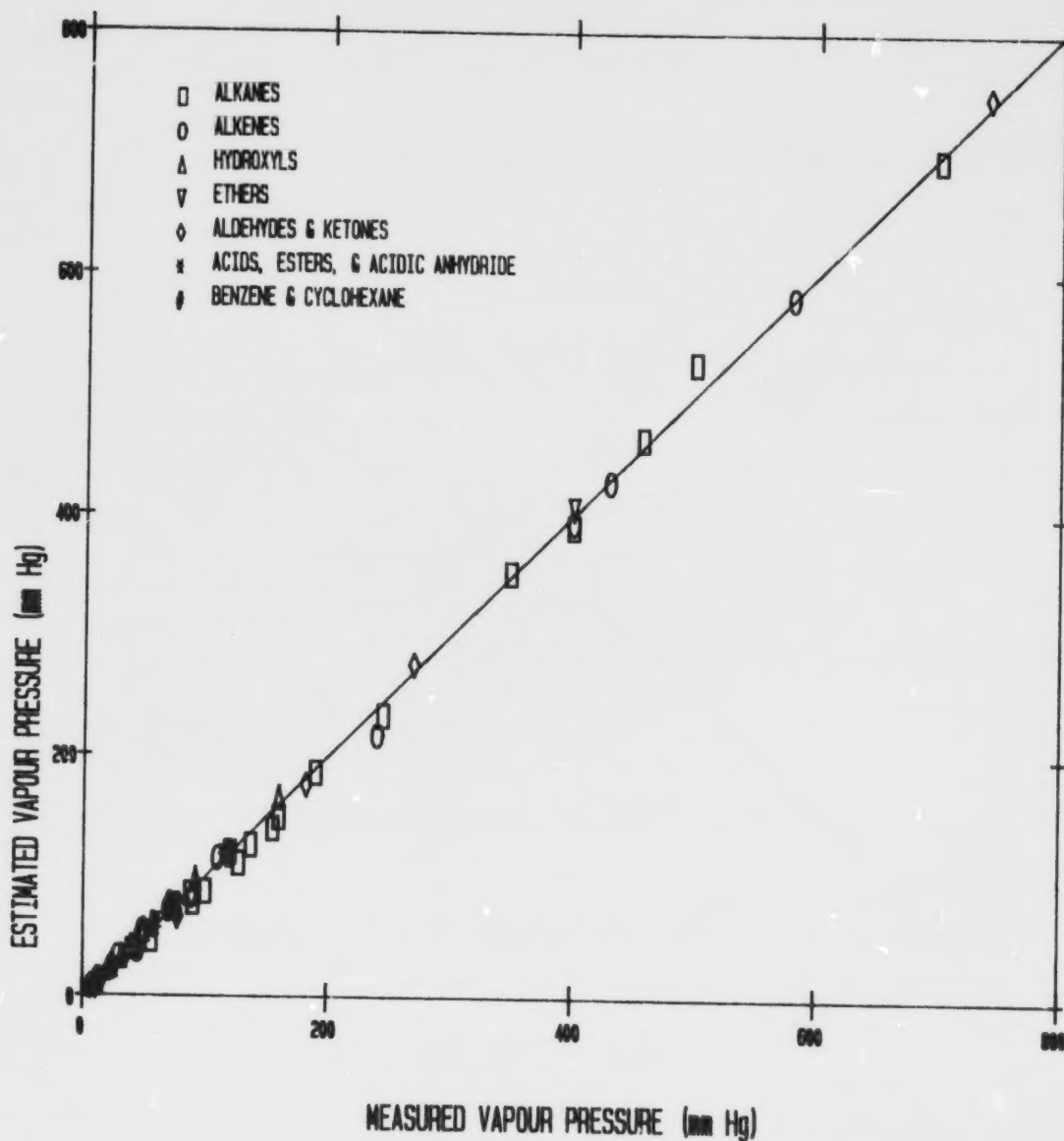
SLOPE OF BEST FIT LINE IS 0.93

INTERCEPT OF BEST FIT LINE IS 0.04

AVERAGE ERROR IS 0.02

AVERAGE % ABSOLUTE ERROR IS 3.7%

FIGURE 3. LIQUID VAPOUR PRESSURE ESTIMATION



NOTES:

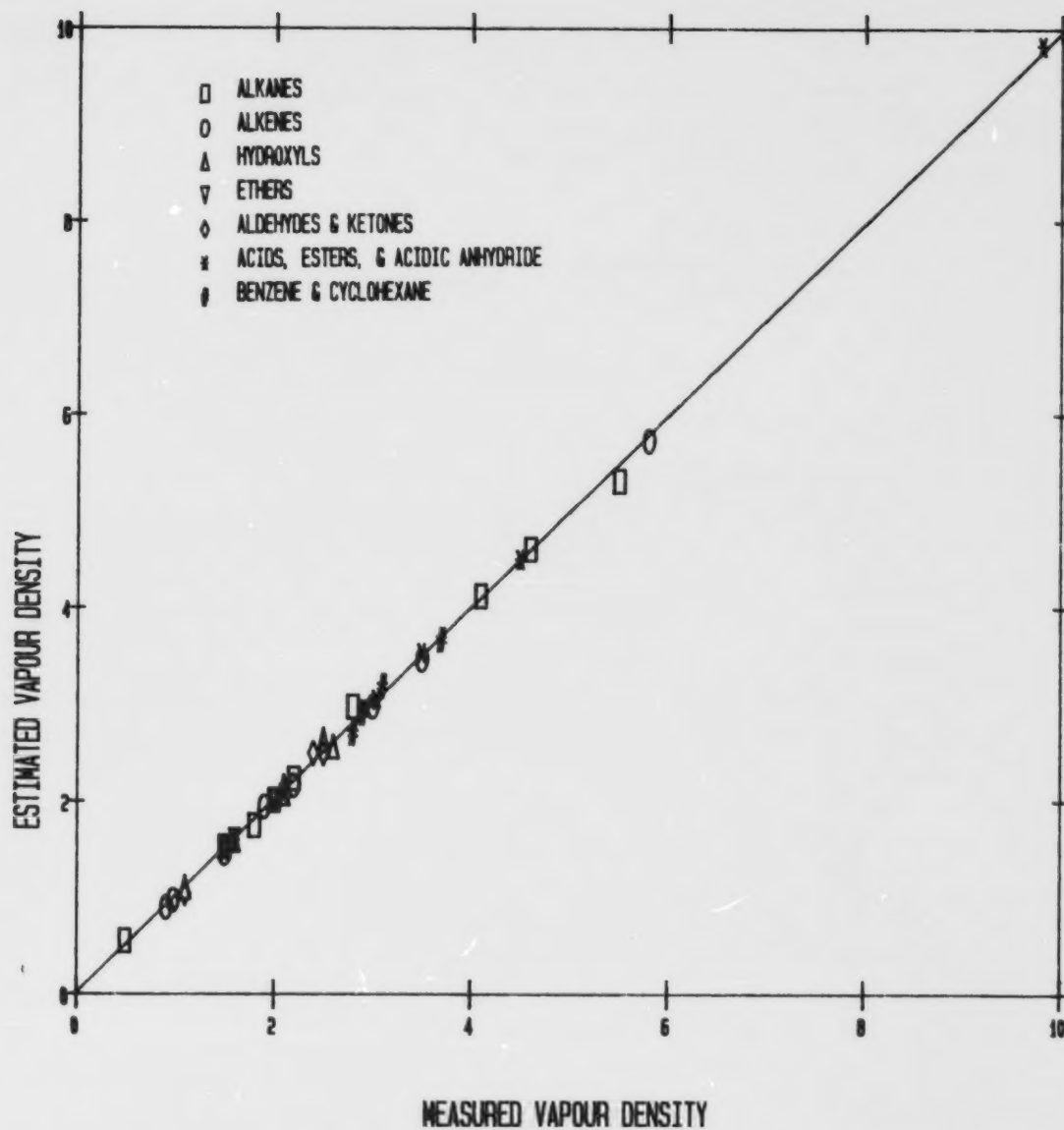
SLOPE OF BEST FIT LINE IS 1.01

INTERCEPT OF BEST FIT LINE IS -2.4

AVERAGE ERROR IS 1.68 mm Hg

AVERAGE % ABSOLUTE ERROR IS 6.9%

FIGURE 4. VAPOUR DENSITY ESTIMATION



NOTES:

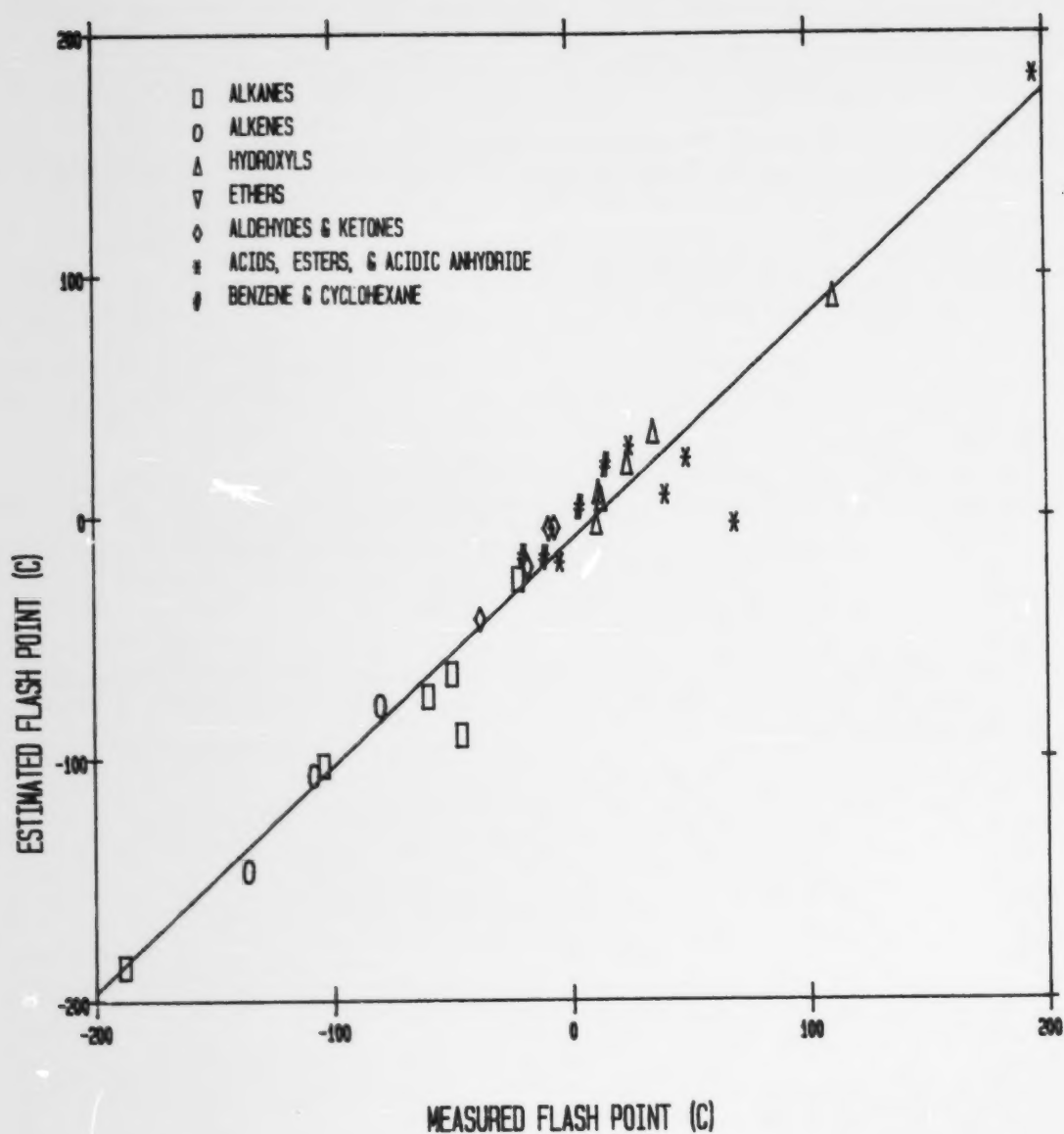
SLOPE OF BEST FIT LINE IS 0.99

INTERCEPT OF BEST FIT LINE IS 0.01

AVERAGE ERROR IS 0.001

AVERAGE % ABSOLUTE ERROR IS 1.9%

FIGURE 5. CLOSED CUP FLASH POINT ESTIMATION



NOTES:

SLOPE OF BEST FIT LINE IS 0.93

INTERCEPT OF BEST FIT LINE IS -10.2

AVERAGE ERROR IS 9.5 C

AVERAGE % ABSOLUTE ERROR IS 4.1%

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LNG SPILL AND DISPERSION MODELLING

E. Alp*, S. Alp, S.G. Guerin, J. Reid**, C.H. Matthias**, D. Napier#, R.V. Portelli

Concord Scientific Corporation
Toronto, Ontario, Canada

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**Atmospheric Environment Service
Environment Canada

#University of Toronto
Department of Chemical Engineering
and Applied Chemistry

Mailing Address:

*Concord Scientific Corporation
2 Tippet Road
Downsview, Ontario
M3H 2V2

1. INTRODUCTION

This paper presents the development of a Liquefied Natural Gas (LNG) spill and dispersion model and its evaluation against field data. The work has been carried out for the Atmospheric Environment Service (AES) by Concord Scientific Corporation (Alp et al., 1984 a, b) under the Energy R & D Program. The objective of this project was to develop a computer program for estimating hazard zones associated with the dispersion of LNG in the atmosphere, and make this program available Canada-wide by implementing it on the AES' computer system in Downsview.

1.1 General

A number of incidents in recent years involving the accidental release into the atmosphere of toxic or flammable heavy gases during their manufacture, storage, or transport have underlined the pressing need by the responsible agencies to be able to plan for and to respond to such emergencies. The derailment of a freight train carrying chlorine and other hazardous materials in Mississauga, Ontario, in November 1979 brought home to Canadians the inherent dangers and the severity of the required responses in such an incident. The recent accident in India with methyl isocyanate is a further example.

One such substance, natural gas, is being used more and more in the world, both as an energy source and as a chemical feedstock. The Dome Petroleum project to export natural gas to Japan from Canada's west coast is an evidence of increased interest worldwide. Natural gas is composed almost entirely of methane, but also contains small amounts of ethane, propane, butane, pentane and nitrogen. It is an odorless hydrocarbon which is not toxic to plants or animals. Methane is flammable, however, when its concentration in air is 5-15 % by volume, and it is this property which makes natural gas a hazardous substance as well as a desirable fuel.

Natural gas in bulk quantities is usually transported by pipeline as a compressed gas. However, for long distances, where it is difficult to build pipelines, such as the stretch of the Pacific Ocean between the west coast and Japan, the most economical way of transporting it is by tankers in liquefied form. LNG is a highly volatile cryogenic substance which has about 1/600th the volume of its gaseous form. Natural gas is usually transported by pipeline to a near-shore facility where it is liquefied by cooling, pumped aboard specially designed and insulated tankers, transported to another port, pumped to an on-shore facility where it is vaporized by warming, and fed into a pipeline system for distribution.

One of the major concerns over this procedure for transporting LNG is the possibility of large spills up to 125,000 m³, which can occur on land in the port facilities, in the harbour, particularly during

transfer procedures, or at sea. Spills could be the result of ship collisions or groundings, natural disasters, design faults, construction or fabrication errors, human error, sabotage, or other causes. Once LNG has spilled, it will evaporate and produce a cold, dense cloud of gas, which will then diffuse and be transported by wind. This cloud of vaporized LNG may ignite if its atmospheric concentration lies between the upper and lower flammability limits, destroying or significantly damaging the ship or facility from which the spill occurred and possibly igniting other buildings or installations which the vapour cloud had drifted over.

To plan for and respond to such occurrences, models for estimating the hazard zones are necessary.

In this project, Concord Scientific Corporation has conducted a survey of potential users in Canada, reviewed the available LNG spill models, and identified state-of-the-art models for simulating the spill, evaporation, and atmospheric dispersion of LNG. A consistent set of equations was adapted and a computer program to compute the hazard zones was implemented. The predictions were compared to data from experiments and the model performance was found to be satisfactory. The model has been implemented on the Atmospheric Environment Service's computer system in Downsview.

This paper presents the user survey and the literature review, the model selection process, the model equations, and the comparison of predictions with data. Recommendations are also presented for future work.

1.2 User Survey

To ensure that during the course of the model development a range of diverse user needs would be taken into consideration, a survey of potential users of the proposed LNG model was conducted. This survey consisted of distribution of a questionnaire and interviews with industry and government representatives who had relevant experience and/or responsibility for LNG spills.

The following provides a summary of the main points derived from the interviews and responses to the questionnaire:

- The majority (>60 %) expressed that a need exists for a proven heavy gas dispersion model. Past conflicts over differing results from different models point to the need for a state-of-the-art model which can be adopted by both industry and government in the assessment of risk from LNG spills.
- The Navigable Water Protection Act, which is administered by the Canadian Coast Guard, requires that a risk assessment and route analysis be carried out before approval can be given, for example, for an LNG port facility and LNG transport

routes. This requires use of models which can simulate LNG spills and resulting hazard zones for estimation of potential impacts/ risks.

- Most felt that needs are just as great or greater for models for other hazardous substances such as H_2S ; therefore priority should be placed on a model or modelling system which could handle spills of various heavy gases (e.g., LPG) as well as other hazardous substances.

2. PHYSICS OF AN LNG SPILL

2.1 Events Following a Spill and Important Phenomena to be Considered in an LNG Spill Model

Liquefied Natural Gas (LNG) is a cryogenic liquid (boiling point $-162^{\circ}C$ at 1 atm) transported under ambient pressure. When spilled on a level surface (land or water), it forms a liquid pool which rapidly spreads due to gravity over a film of vapour. This vapour film is formed by boiling of the LNG due to heat transfer from the surface. Evaporation also occurs at the interfaces with the surrounding air.

The vapour formed by the boiling LNG is initially denser than air because of its low temperature. This dense gas spreads due to gravity and diffuses into the surrounding air due to atmospheric (top and edges of the cloud) as well as rolling-front (edges of the cloud) turbulence. The cloud is also advected under the influence of wind. The wind profile and the atmospheric turbulence are modified by the presence of the dense cloud. Heat is transferred from the surface to the cloud and by entrained air into the cloud. The humidity in the entrained air results in condensation within the cloud, which provides a further source of heat to the dense gas. The dense gas eventually becomes both diluted and warmer such that first non-buoyant and then buoyant atmospheric dispersion takes place (natural gas is lighter than air at ambient temperatures).

The above description of events after an LNG spill points to the important phenomena which have to be taken into account in an LNG dispersion model.

The above events may be considered in two distinct phases. The first phase covers the stages while the spilled LNG is still in the liquid phase (spill stage, pool formation stage, pool spread stage, evaporation stage). The second phase covers the stages while the LNG is in gaseous form (heavy gas dispersion stage, non-buoyant and buoyant dispersion stage).

An LNG spill model would then consist of two modules, one module for each of the two phases. A general schematic of required modules and sub-modules of an LNG spill is shown in Figure 2.1. Because the second phase events may affect the first phase events (e.g.,

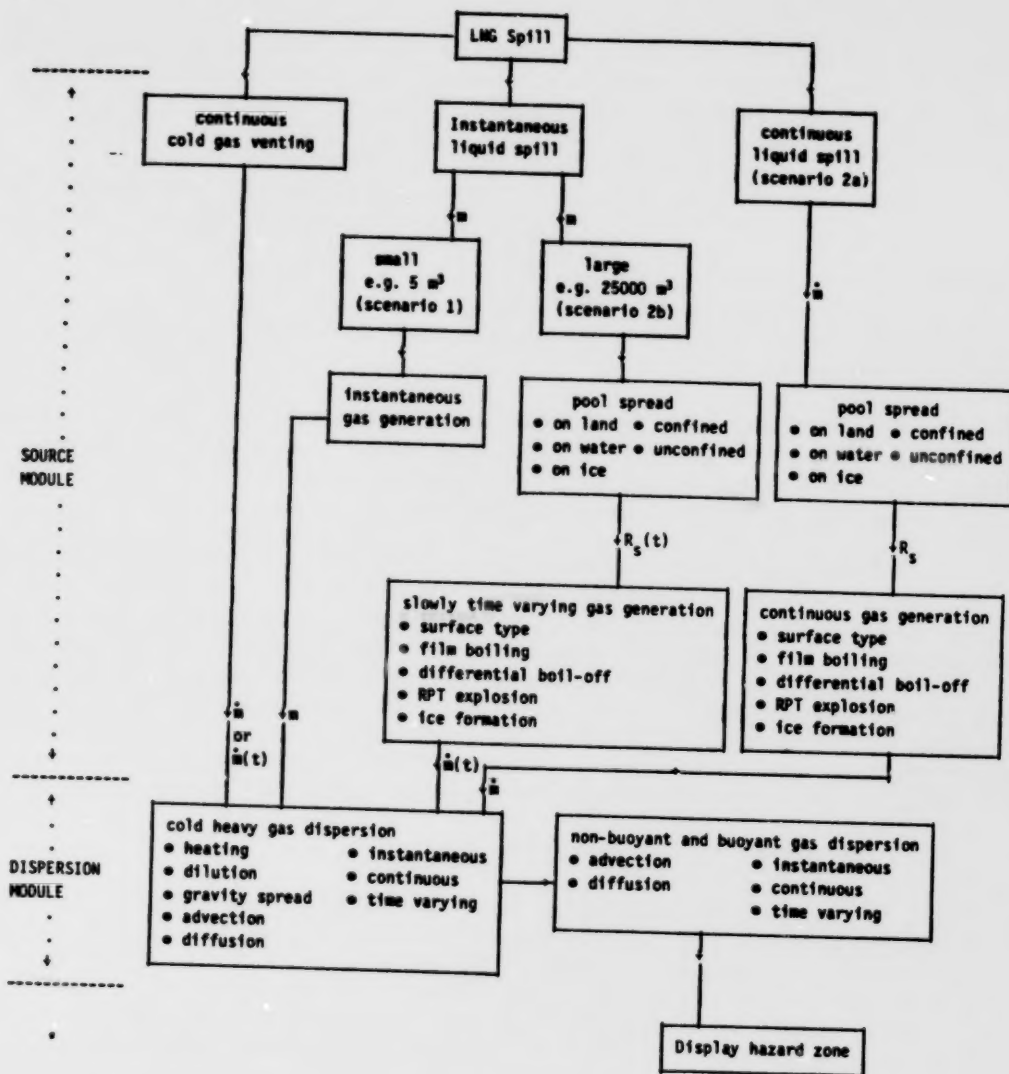


FIGURE 2.1

General Schematic of an LNG Spill Model

(m = mass, $\dot{m}$ = mass per unit time, R_s = liquid pool radius, t = time)
 •'s indicate phenomena that should be considered in a given module, (note that some combinations might not be possible).

heavy gas modifying the atmospheric flow field locally and hence the turbulence and, in turn, evaporation rates), an ideal model should have these two modules coupled. This would, however, complicate the model significantly.

In general, two types of liquid spill may be envisaged: A continuous liquid leak (which may develop, for example, during transfer of LNG from a marine tanker to a land based storage tank), or a catastrophic spill (which may develop as a result of collision of a marine tanker). Furthermore, spills could be on open water, ice or land, could be confined (e.g., a diked plant site), or semi-confined (e.g., harbour), or under water.

It is clear that spill scenarios are numerous, and it is not the purpose of this project to analyze these in detail. We shall concentrate on a scenario where large quantities of LNG in liquid form are spilled on open water (Scenarios 2a and 2b in Figure 2.1).

In general, there are two basic formulations for dispersion of gases in the atmosphere (instantaneous or continuous gas production). If the gas release duration is short relative to the time it takes for the gas to reach its maximum hazard zone limits, then the gas production may be considered as instantaneous for the purposes of modelling dispersion in the atmosphere. If the gas release duration is long relative to the time it takes the gas to reach maximum hazard zone limits, then the gas production may be considered as continuous. Our selected scenario will require the dispersion to be modelled as a continuous gas release.

2.2 Pool Spread and Evaporation Models

A survey of available pool spread and evaporation models indicated a general lack of models which can systematically treat the possible spill scenarios. A matrix of these scenarios and the respective applicable models and input requirements is presented in Table 2.1. It is quite clear that state-of-the-art practical gas generation flux ($\dot{m}$) models are simply empirical constants for given surfaces and the detailed physics of film boiling is not considered (there has been research on the detailed physics; however they are not utilized in practical applications).

In general, the amount of liquid remaining on the surface $V [m^3]$ can be expressed based on an integral mass balance of the spilled liquid (Briscoe and Shaw, 1980):

$$V = V_i + \int_0^t \dot{V}_C dt - \frac{m}{\rho} \quad \dots(2.2.1)$$

where V_i = instantaneously spilled volume [m^3].

$\dot{V}_C$ = volumetric spill rate, which may be a function of time [m^3/s],

TABLE 2.1

Calculation of Pool Spread (R_s = Pool radius):
Applicable Models and Their Input Requirements

	instantaneous liquid spill (scenario 1)	continuous liquid spill (scenario 2a)	large instantaneous or time varying liquid spill (scenario 2b)
<u>On Water</u>			
Open	Opschoor, LNGVG or * $m, \dot{m}$	LNGVG or * $\dot{m}, \ddot{m}$	LNGVG or * $\dot{m}(t), \ddot{m}$
Confined (area A)	Opschoor or * $m, \dot{m}(t), A$	NA $\dot{m}, \ddot{m}(t), A$	NA $\dot{m}(t), \ddot{m}(t), A$
<u>On Land</u>			
Open	B & S $m, \dot{m}(t), T_{\text{soil}},$ soil properties	B & S $\dot{m}, \ddot{m}(t), T_{\text{soil}},$ soil properties	B & S $\dot{m}(t), \ddot{m}(t), T_{\text{soil}},$ soil properties
Confined (area A)	NA $m, \dot{m}(t), T_{\text{soil}}, A,$ soil properties	NA $\dot{m}, \ddot{m}(t), T_{\text{soil}}, A,$ soil properties	NA $\dot{m}(t), \ddot{m}(t), T_{\text{soil}}, A,$ soil properties
<u>On Ice</u>			
Open	NA	NA	NA
Confined	NA	NA	NA
<u>Under Water</u>	not available	not available	not available

Notes:

* May also be obtained as a special case of B & S (Briscoe and Shaw, 1980)

NA Model not available, but may be derived based on B & S and principles of heat transfer

Opschoor (1980)

LNGVG = Stein (1978)

t = time from spill [s],
 m = total mass evaporated during time t [kg],
 ρ = density of liquid [kg/m³].

Assuming a cylindrical shape for the liquid pool,

$$h_s = \frac{V}{\pi R_s^2} \quad \dots(2.2.2)$$

where R_s = liquid pool radius [m],
 h_s = liquid pool height [m].

Due to the very rapid spread of LNG over a flat surface, the cylindrical shape assumption, which is implied by symmetric spread about the spill point, is reasonable.

The rate of spread of the pool is related to the height of the liquid, which provides the gravitational driving force, in the following approximate manner,

$$\frac{dR_s}{dt} = (c_1 g \Delta h_s)^{1/2}, \quad \dots(2.2.3)$$

where g = gravitational constant, 9.81 m/s²,
 $c_1 = 2$, a dimensionless factor to take account of the fact that the liquid inertia is equal to only a fraction of the inertia of the whole liquid-pool mass moving with the acceleration at its leading edge,
 $\Delta = (1 - \frac{\rho}{\rho_{\text{surface}}})$, a dimensionless parameter to take into account the displacement of the surface by the weight of the LNG pool; for spills on water ρ_{surface} is the density of water, for spills on land $\rho_{\text{surface}} \gg \rho$, therefore Δ is taken as 1.

This formulation is essentially for the travel of a density front, and requires $R_s \gg h_s$, which is a reasonable assumption for the spread of LNG on a relatively hot surface.

The total mass evaporated during time t can be calculated from

$$m = \int_0^t \dot{m} dt \quad \dots(2.2.4)$$

where $\dot{m}$ = evaporation rate [kg/s].

Specification of $\dot{m}$ is very critical in closing the above equation set, Equations 2.2.1 - 2.2.4. This equation set constitutes a

general model for describing the pool spread and evaporation of LNG spills (or any cryogenic substance, with the proper choice of the empirical parameters).

The evaporation rate $\dot{m}$ can be calculated in the following manner, assuming heat transfer from the water surface to the LNG pool is the limiting factor in evaporation.

$$\dot{m} = \dot{m}'' \pi R_S^2$$

where $\dot{m}''$ = an empirical evaporation flux in terms of mass per unit time per unit area, specification of which still carries some controversy; it is usually taken between 0.05 kg/(m²·s) and 0.2 kg/(m²·s).

For unconfined spills on water, no ice formation on the water surface is expected; for confined spills, however, transition from film boiling to nucleate boiling may occur, and a solid ice layer may form (Opschoor, 1980; Waite et al., 1983).

Differential boil-off of LNG constituents is a further complicating factor, which is important especially for instantaneous and finite time releases of LNG, since changing concentrations of the various constituents will change the thermodynamic properties of the liquid and hence heat transfer and evaporation rates (Stein, 1978; Waite et al., 1983). For non-continuous releases, an empirical minimum pool thickness, after which the pool breaks up, must be incorporated into the model, along with a suitable heat transfer and evaporation rate model.

The development of source modules for LNG spills is an ongoing research activity (Waite et al., 1983; Jensen, 1983) and a more comprehensive source model development program is recommended for implementation of the LNG dispersion model. It should be noted that effects of, for example, waves, in accident situations, have not yet been considered in any of the available models.

3. LITERATURE SURVEY AND DISPERSION MODEL SELECTION

Through a literature search (on-line, manual, and interviews) ~35 chemical dispersion models have been identified, some of which have been specifically designed for heavy gases, and some for LNG. These models fall into five basic categories (in the order of increasing complexity):

1. Simple Gaussian formulations: Most of these are dispersion modules of more general chemical spill hazard assessment systems. Some examples are: SPILLS (Fleisher, 1980); SPILL (Zimmerman, 1981); SINST (Whitacre, 1978); HACS (Raj and Kalelkar, 1974; Raj and

O'Farrell, 1975; Potts, 1981; Colonna, 1982; Havens, 1983) and May et al., 1973. This list is by no means exhaustive. However, none of the Gaussian formulations represents the state-of-the-art in LNG dispersion modelling. Therefore they were not considered to be serious candidates for the purposes of this project.

2. Box models. These models essentially treat the cold heavy gas as a cylinder of uniform properties. The cylinder of gas is advected by the ambient wind, spread by gravity and diluted by entrainment of air. Some examples are: Germeles and Drake, 1975; van Ulden, 1974; Fay, 1980; Cox and Roe, 1977, Cox and Carpenter, 1980, Bradley et al., 1983; Eidsvik, 1980, 1981, Fay and Ranck, 1983; van Buijtenen, 1980; Fryer and Kaiser, 1979; EASE - Tran and Vazirinejad, 1981. Of these, Germeles and Drake, Cox and Carpenter, Eidsvik, and EASE models claim that they can treat both instantaneous and continuous releases. Only the Eidsvik model provides a smooth transition from gravity spread stage to non-buoyant dispersion stage, which is considered to be an important criterion (Bradley et al., 1983; Havens, 1982). Hence, Eidsvik's model seems to be the top contender among the "box" models. It has also been independently tested by Havens (1982) and Woodward et al. (1982).
3. Advanced Similarity Models These models assume similarity profiles for distributions within the heavy gas cloud unlike the uniform profiles assumed in the box models, which may themselves be considered simple similarity models. Some examples are: Colenbrander, 1980, Colenbrander and Puttock 1983 a,b; Fannelop, 1982 (see Jagger, 1983); Flothmann and Nikodem (1980). Of these, only the Colenbrander model has been critically compared with experimental data. It is also the best documented model (Havens and Spicer, 1983). On the other hand, it is continuously being modified and updated (Colenbrander and Puttock, 1983a; Havens, 1983).
4. Models based on layer averaged conservation equations. These models utilize sets of first order partial differential equations describing conservation of mass, momentum and energy. The overall objectives of the present project preclude implementation of such a model: Zeman (1982); SLAB (Ermak et al., 1982); van Ulden (1979). Only the SLAB model has been compared with LNG spill experiments. It is based on Zeman's model.
5. Models based on three-dimensional conservation equations. These models employ 3-D partial differential equations describing conservation of mass, momentum and energy. The overall objectives of the present project preclude implementation of such a model: FEM3 (Ermak et al., 1982); SIGMET (Havens, 1982); ZEPHYR (Woodward et al., 1982); MARIAH (Woodward et al., 1982); TRANSLOC (Schnatz & Flothmann, 1980); DISCO (LNG, 1975); SMART (Tran and Liu, 1981); MINT/TDC (see Bowman, 1978).

The overall philosophy behind the literature survey was not to examine exhaustively the available models, but rather to select quickly a short list, based on easily identifiable criteria such as being state-of-the-art, practical applicability, having been tested against experimental data, available documentation, as well as scientific soundness in the way they treat the important phenomena in an LNG spill, and then to examine further the short-listed models for final selection.

It has already been mentioned that the state-of-the-art practical LNG dispersion models belong to the second and third categories. The best models in these two categories are Eidsvik's and Colenbrander's models, respectively. These two models will now be further examined.

Based on a more extensive review of the available literature on Eidsvik's and Colenbrander's models, their major characteristics are summarized in Table 3.1. Clearly, Colenbrander treats the basic flow and dispersion processes in a more detailed way, especially with the use of more detailed similarity profiles. Also, treatment of the source by considering the development of a gas blanket over the liquid pool is unique to this model. Some of the fine tuning features, like the effect of moisture and heat transfer from the ground to the gas cloud, are only recently being considered for the Colenbrander model (Colenbrander and Puttock, 1983a; Havens, 1983) and are not available in the original version. Eidsvik's model is based on an instantaneous release of gas, does not consider development of a gas blanket over the source, and its use is questionable for finite time or continuous releases. Colenbrander's model, on the other hand, is based on a continuous release, finite time releases being handled through a quasi-steady treatment. Based on the scenarios discussed in Section 2, an instantaneous release of gas (not liquid) is only likely through a catastrophic spill of a small amount of liquid, such as from a tanker car, and in Canada such transportation is not a commonly practised mode. Hence, from the point of view of possible scenarios, Colenbrander's model is more suitable for the purposes of this project. Neither model is suitable in calm wind situations for finite time releases. A recent model by Byggstoyl and Saetram (1983) may be used to complement the selected model in calm wind situations. Input requirements of both models are comparable. Cost of implementing and also running of Colenbrander's model is more than Eidsvik's but probably of the same order of magnitude.

Based on the selection criteria mentioned before, Colenbrander's model was selected for final implementation.

TABLE 3.1
Review of Major Model Characteristics

	<u>EIDSVIK</u>	<u>COLENBRANDER</u>
vertical wind profile	uniform	power law
concentration	uniform	uniform with Gaussian edges
entrainment	entrainment velocities	through "K" theory
gravitational spread	symmetric about centre of mass, frontal speed	crosswind direction only, frontal speed
energy balance		
latent heat of droplets	considered	not considered
latent heat of moisture	considered	considered
heat transfer from below	forced convection	forced or free convection
100 % gas blanket over source	not considered	blanket spread symmetric about stationary source
applicability to various gas release scenarios		
instantaneous (Scenario 1)		
calm	yes	no
wind speed >2m/s	yes	questionable
continuous (Scenario 2a or 2b)		
calm	no	no
wind speed >2m/s	questionable	yes

4. DETAILED DESCRIPTION OF THE ADAPTED DISPERSION MODEL

4.1 The Steady State Model

The model treats dispersion of gas released from an idealized rectangular-shaped source of half width $y = B$ and length L (in the downwind direction), with the gas source center at the origin of a Cartesian coordinate system as shown in Figure 4.1. Similarity forms for the concentration profiles are assumed which represent the plume as being composed of a horizontally homogeneous section in which dispersion only occurs vertically, with Gaussian (concentration profile) edges. A power

law wind velocity profile is assumed. With the assumed similarity forms for the concentration (c) and velocity (u) profiles (see Figure 4.1), the variables c_A (ground level, centreline gas concentration), b (half-width of the horizontally homogeneous center section of the plume), and s_y and s_z (scale factors in the similarity forms for concentration) are constrained by ordinary differential equations. These are based on the vertical diffusion equation for turbulent diffusion in the z-direction,

$$u_x \frac{\partial c}{\partial x} = \frac{\partial}{\partial x} (K_z \frac{\partial c}{\partial z}), \quad \dots(4.1.4)$$

a gravity intrusion relation,

$$\frac{d B_{EFF}}{dt} = k' \sqrt{g \left(\frac{\rho_{plume} - \rho_{air}}{\rho_{plume}} \right) H_{EFF}}, \quad \dots(4.1.2)$$

which represents the lateral gravity spread of the heavier-than-air gas plume, and the lateral diffusion equation for horizontal turbulent diffusion in the lateral direction,

$$u_x \frac{\partial c}{\partial x} = \frac{\partial}{\partial y} (K_y \frac{\partial c}{\partial y}). \quad \dots(4.1.3)$$

At downwind distance x_t where b has decreased to zero, the cross wind concentration profile is assumed Gaussian and gravity spreading is terminated.

For a steady gas/air plume, the centreline concentration is determined from the material balance

$$E = \int_0^\infty \int_{-\infty}^\infty c u_x dy dz \quad \dots(4.1.4)$$

where E is the plume gas source strength determined as described below.

These equations are combined with an equation of state relating cloud density to gas concentration and are solved simultaneously to predict s_z , s_y , c_A and B_{EFF} as functions of downwind distance beginning at the downwind edge of the gas source.

4.2 Calculation of the Source Strength and Initial Conditions

Let $\dot{m}^*$ be the evaporation flux in the liquid pool. Let Q_{max}^* be the maximum possible gas take-up flux into the atmosphere by the advecting wind consistent with the assumed similarity profiles. Let Q^* be the actual gas take-up flux depending on the actual conditions of the particular spill. If $\dot{m}^* > Q_{max}^*$, a pure gas blanket with concentration

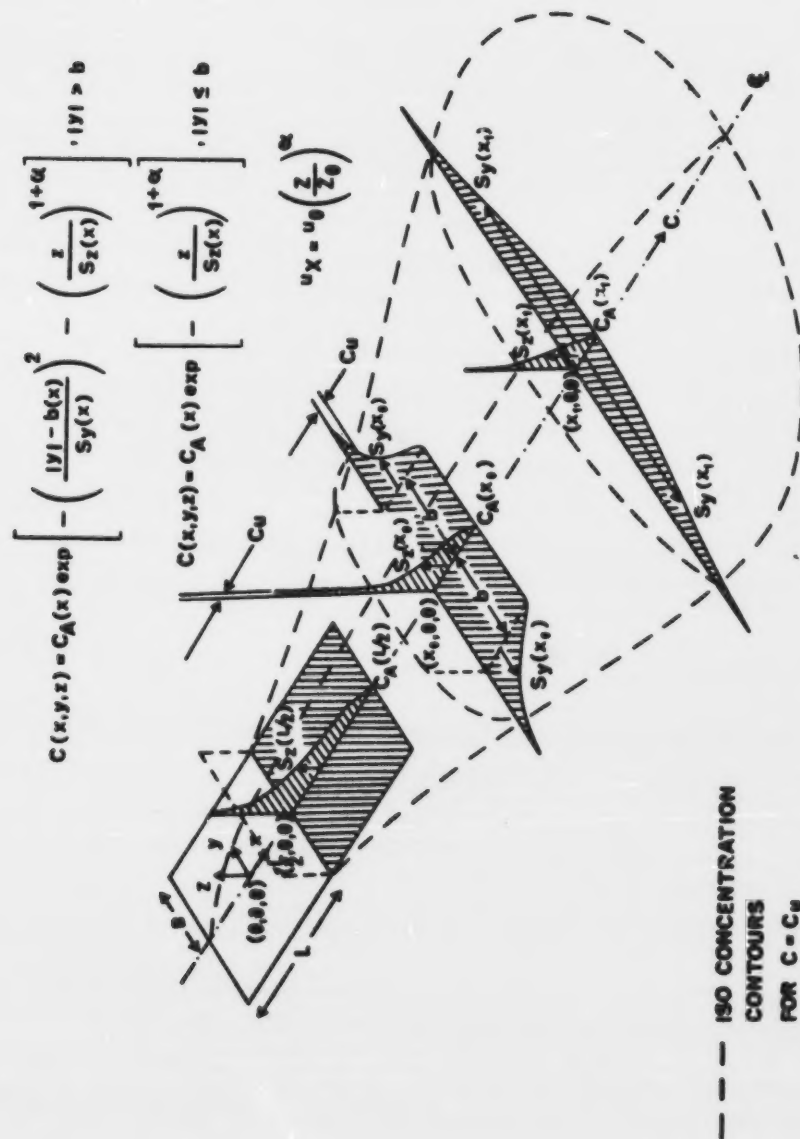


FIGURE 4.1

Representation of Concentration and Velocity Profiles Downwind of an Area Source

$C_A = \rho_E$ (density of pure gas) will form over the source, then Q^* should be taken to be equal to Q_{max} . If $\dot{m}^* < Q_{max}$, no gas blanket forms over the source, and $Q^* = \dot{m}^*$. This type of treatment of the source flux is unique to Colenbranders's model.

The source strength E is calculated using this Q^* and the size of the gas source based on material balances by integrating appropriate forms of the transport and diffusion equations similar to the ones given in the previous section from the upwind edge of the source to the downwind edge. These integrations also provide the initial conditions for the dispersion equations of the previous section at the downwind edge of the source.

4.3 Quasi-Steady Approximate Treatment of Transient Gas Releases

The model also treats transient gas releases, i.e., releases in which the area of the gas source and/or the gas emission rate vary with time. This is accomplished by using "observers" which take up gas as they pass over the gas source. A steady state calculation is then made for each observer. By knowing the location of each observer as a function of time, it is possible to determine hazard zones due to contributions from successive "observers" at any desired time.

4.5 Equation of State for Cloud Density

The cloud density at any downwind distance within the plume is calculated using a thermodynamic subroutine based on an energy balance which takes into account the heat transfer from the ground, the heat of condensation from the humidity that is present in the entrained air, and the temperature of air and surface. This requires that the energy equation be solved simultaneously with the transport, diffusion and spread equations presented in Section 4.1.

5. MODEL RESULTS

The steady state portion of the adapted model was implemented on the AES' AS/6 computer using FORTRAN 77. The model was then tested through sensitivity runs and 13 validation runs against published 1980 experimental data from Maplin Sands, as well as against published predictions of the two versions of Colenbrander's model (Puttock et al., 1983, and Colenbrander and Puttock, 1983a). The validation run results are summarized in Table 5.1. A 5% lower flammability limit was used for defining the hazard zone for comparison purposes. Normally 50% of the LFL would be taken for defining hazard zones in order to account for pockets within the plume.

Two simple error statistics have been computed for both these models. For a sample size of n points the mean relative error is defined by

TABLE 5.1

Summary of Results

Run #	U ₉ (m/s)	Hazard Zone Length (5%)(m)			
		Experiment (Puttock et al. 1983)	Present Prediction	Puttock et al. 1983 Prediction	Colenbrander and Puttock, 1983b Prediction
9	8.9	135 ± 15	111	125	90
12	1.5	63 ± 4	36	200	45
15	3.6	165 ± 15	73	250	100
27	5.5	190 ± 20	129	260	235
34	8.6	150 ± 20	160	195	185
35	9.8	175 ± 25	189	205	205
39	4.1	130 ± 20	148	355	270
56	5.1	110 ± 30	82	210	115
29	7.4	140 ± 15	185	250	245
MRE% (exclude #12) MARE% (" ")		- -	- 8.80 23.97	+ 58.83 60.68	+ 22.33 40.52

$$MRE = \frac{1}{n} \sum_{i=1}^n \frac{P_i - O_i}{O_i},$$

where P_i are the individual predictions and O_i are the observations. MRE indicates how well the model performs on the average.

Mean absolute relative error is defined by

$$MARE = \frac{1}{n} \sum_{i=1}^n \left| \frac{P_i - O_i}{O_i} \right|.$$

MARE indicates the effect of sign cancellation when compared with MRE.

Note that the run for $u_0 < 2$ m/s is excluded since the model is not considered valid under calm conditions. Further statistics are not warranted due to the very small number of experiments considered ($n=8$).

Figures 5.1 and 5.2 are two sample figures showing the maximum concentrations observed in two experimental spills as well as the corresponding predictions by the present model. The present predictions clearly match the others quite well. Figure 5.3 shows the approximate lower flammability limit contour for the spill corresponding to Figure 5.2. Again, although somewhat smaller, the presently predicted hazard zone is quite similar to the others.

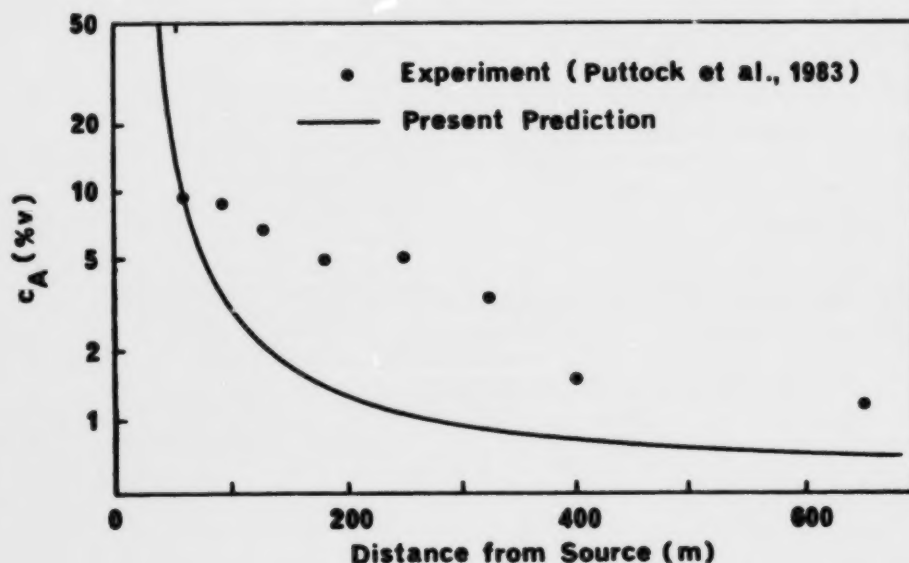


FIGURE 5.1

Maximum concentrations c_A for spill 15 of the reference.

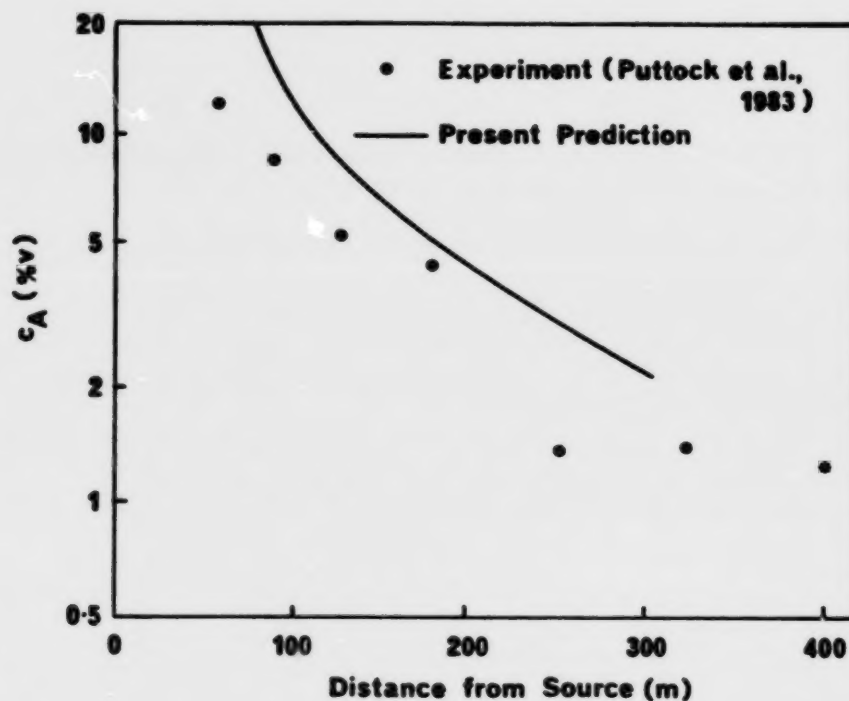


FIGURE 5.2

Maximum concentrations c_A for spill 29 of the reference.

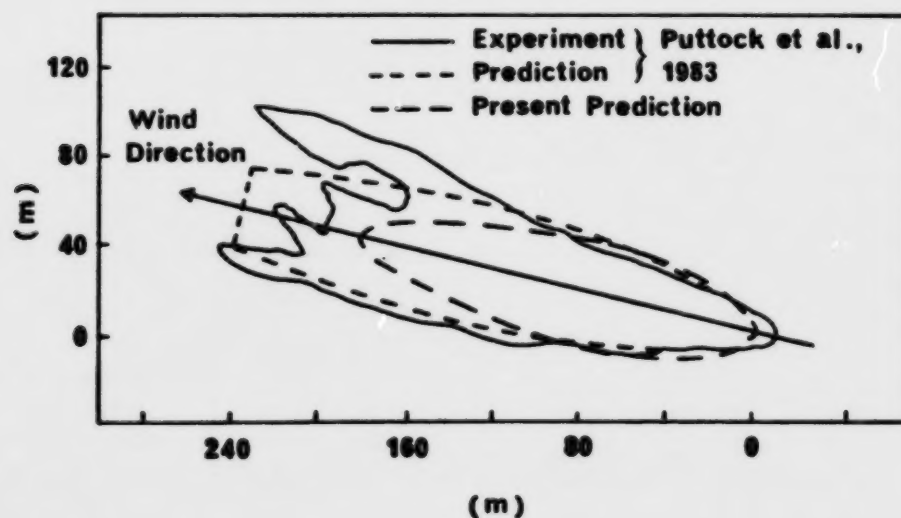


FIGURE 5.3

Plan view of a sample plume from an LNG spill
(spill 29 of the reference)

6. CONCLUSIONS AND RECOMMENDATIONS

A review of available LNG spill and dispersion models was made, a state-of-the-art dispersion model was selected based on the user community needs determined from a survey, the model was then adapted for present purposes, and successfully implemented on the computer.

The model predictions were compared to a series of experimental data and an earlier reported version of the model. Its performance was found to be satisfactory (predicted hazard zone dimensions within ~ 60% of experimental data).

Throughout the user and literature survey, model adaptation, and model running stages of the project, specific needs of the potential user community were kept in mind and weaknesses in available models were identified. These areas are identified below in the form of specific recommendations, for improvement and generalization of the implemented model, as well as for better responding to user community needs.

1. The user survey has indicated a need for a general heavy gas dispersion model. Unfortunately, the scenarios for different heavy gases, their pool formation and vaporization characteristics, etc. are usually very different from each other and therefore it is difficult to develop a generalized model. It would be more cost-effective and also practically acceptable to develop different modules for different substances, especially for the first phase of events after a spill, and utilize them in a general model framework. It is recommended that, based on the experience gained through the implementation of the model in this project, a modelling system framework be developed specific to heavy gases. Such a framework can later be extended to other hazardous substances (toxic or flammable) to form a comprehensive safety assessment modelling system for the majority of hazardous substances manufactured and transported in Canada.
2. It is common practice to test the effects of possible errors in various input parameters and other constants in the model. For example, wind speed measurement is usually only accurate to $\pm 3\%$ to 10% , depending on the quality of the instrumentation used. It is recommended that these possible error bands be determined for each of the parameters in the model, and the predictions examined for such changes in these parameters. This will lead to the identification of important parameters in the model, and indicate the areas which need improvement. Such an investigation has already been done in the present study for the vapour generation flux $\dot{m}''$ and spill rate $\dot{V}_C$; however extension to other parameters is recommended.

3. The weakness of the available models for calm wind situations had been identified early on in the project. It is recommended that the viability of incorporating a sub-model developed specifically for such situations (e.g., Byggstoyl and Saetran, 1983) be investigated.
4. Investigation of the viability of including other mechanisms such as gravity spread in the direction of the wind is not recommended due to the limitations on the existing model theory.

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DETERMINATION OF BURN RATE AND SOOT FORMATION DURING COMBUSTION OF
SOLVENTS COMMONLY CARRIED BY RAIL.

R. Del Delumyea*, Kathy P. Moore, George I. Miller,
Sandra A. Dukes and M. Anne Morgan

Department of Chemistry and Geology
Clemson University
Clemson, SC 29630

and

Gerald Meier

Research and Test Department
Association of American Railroads
Washington DC

ABSTRACT

The amounts of soot produced, heats of combustion, and product consumption rates for several commonly-carried commodities under conditions of varying oxygen availability were measured under controlled conditions. The possibility of obtaining a predictive model for burnrate or amount of soot generated based on physical parameters of the solvent is explored.

INTRODUCTION

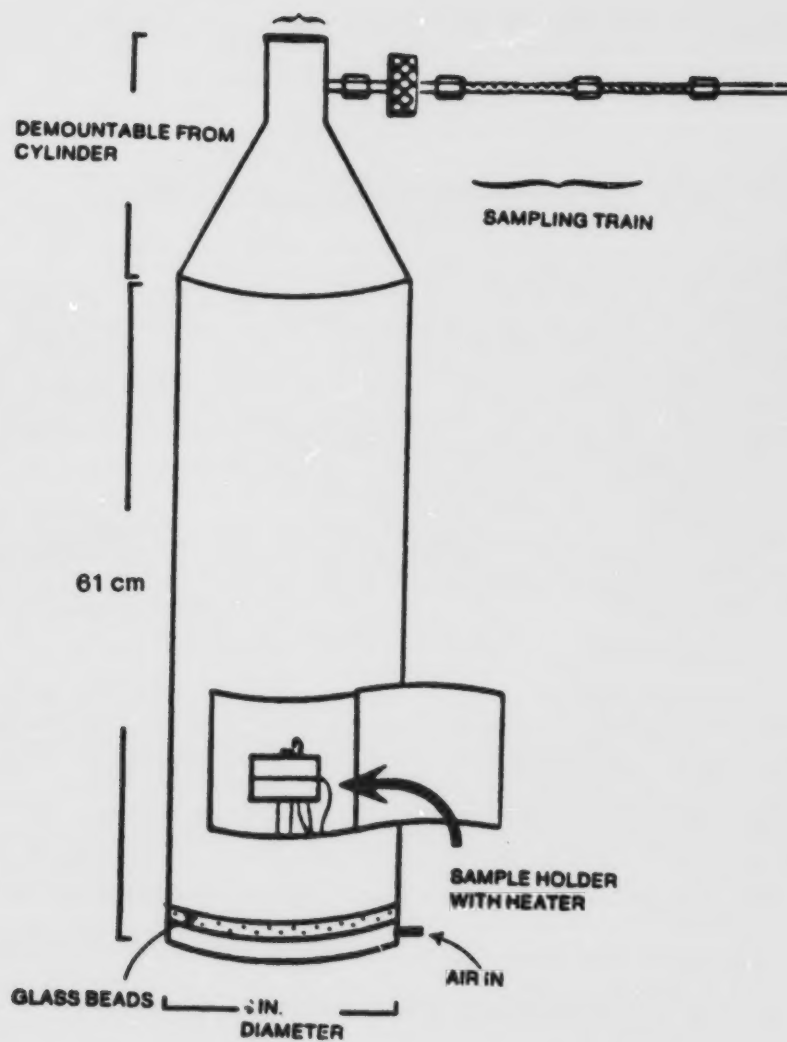
According to the "1984 Emergency Response Guidebook"¹ issued by DOT to personnel responding to rail accidents, the procedure for serious fires of over 60% of the materials is to evacuate personnel in the immediate vicinity and areas downwind and to let the fire burn itself out. Two pieces of data required to evaluate the "Let-Burn Scenario" are: a) the products of combustion, to assess toxicity of the plume and permit estimation of a safe evacuation distance; and b) how fast the fuel is consumed, to determine how long the fire will last.

Two sets of experiments were required to obtain the necessary information on the combustion properties of the solvents and the effects of the conditions surrounding the burn. Calorimeter studies were performed to determine the effects of oxygen availability on the heats of combustion and the amounts of soot produced from combustion of organic solvents. In the other set of experiments, a combustion chamber was constructed to permit control of burn conditions. Using it, solvents were burned and the rates of solvent consumption (burnrates) determined. Trends in the data will be presented and the correlation of the results with physical properties of the solvents will be discussed.

EXPERIMENTAL

Calorimetry. A Parr Model 1341 Oxygen Bomb Calorimeter, standardized with benzoic acid, was used in this study. The system was calibrated using ASTM D-240. This procedure was modified for studies of reduced oxygen availability by reducing the pressure of oxygen used to charge the calorimeter from 30 atmospheres to as low as 1.2 atm.

Open-Burn System. The combustion chamber, described at the 1984 Technical Seminar on Chemical Spills, is illustrated in the figure. It consisted of a 0.64 cm stainless steel cylinder, 20 cm ID and 61 cm in height. A demountable stainless steel funnel which terminated in a 3.5 cm ID tube was affixed to the top. Pressurized laboratory air was passed through desiccant and (4) angstrom molecular sieve before entering a gas-dilution manifold which consisted of a set of flowmeters



and precision metering valves. A 7.00($\pm$ 0.05) ml aliquot of the solvent to be burned was transferred volumetrically to a platinum crucible. The crucible rested in a 7.5x10x5 cm aluminum block fitted with a resistive heater to control the sample temperature prior to ignition. A nichrome igniter wire ran through the block to a position above the sample well. The burn was initiated using a variac to increase the igniter wire voltage until the sample ignited, as indicated by the thermocouple above the sample, which was monitored during the burn.

RESULTS AND DISCUSSION

Calorimetry. Table 1 lists the heats of combustion for several commodities commonly carried by rail under conditions of varying oxygen pressures added to the bomb calorimeter. The effect of oxygen availability on the heat of combustion is as expected for most compounds. The general trend is an increase in the heat released as the air-to-fuel ratio increases. Oxygen-containing species were less seriously affected by reduction in oxygen availability than other classes, as shown in the data in column 8 of Table 1. This value represents the percent decrease in the heat of combustion from 30.2 to 5.2 atm of oxygen. The effect of intramolecular oxygen is to significantly reduce the effect of changes in the externally-supplied oxygen. Aromatic species exhibited the most significant decrease in the heat of combustion; however, phenol, which contains oxygen was the least affected aromatic. All of the solvents tested failed to burn to completion between 1 and 5 atmospheres.

Table 1. Heats of Combustion (cal/g) Under Differing Conditions of Oxygen Availability.

Compound	Lit Value	Atmospheres of Oxygen					% Change
		30.2	20.2	15.2	10.2	5.2	
Methanol	5417	5450	5433	5382	5250	5385	1
2-Propanol	7899	7913	7942	7884	7863	5662	28
1-Butanol	8628	8586	8543	8423	8427	5818	33
Ethyl Acetate	6093	5977	6051	5966	5958	5461	10
Vinyl Acetate	--	5446	5703	5714	5710	5550	-2
Butyl Acetate	7295	7405	7315	7353	7276	5997	18
MEK	8100	8000	7978	7949	7916	6237	23
MIBK	--	8918	8888	8827	8772	5625	37
Butyraldehyde	--	8005	8075	8078	8035	5513	31
Acetone	7367	7319	7344	7258	7338	5144	30
Acrylonitrile	7931	7846	7796	7846	7980	6107	23
Chloroform	747	1007	NB	NB	NB	NB	--
Hexane	11546	11426	11410	11459	10745	5964	48
Cyclohexane	11132	11038	11041	11082	10349	5987	46
Benzene	10012	9983	9979	9823	9208	6173	38
Toluene	10154	10089	10098	10068	8464	5365	47
Xylenes(1)	10268	10155	10204	10045	8629	5153	50
Aniline	8728	8631	8659	8630	7252	5234	40
Styrene(2)	10054	9959	10065	9954	8952	5160	49
Phenol	7764	7656	7680	7712	7492	6052	22

1. Literature value is average of the three isomers.
2. Sample at 35 degrees C.

The amount of soot formed during combustion of the solvents was calculated from the weight of the residue in the calorimeter. The percent of original mass present was termed the "% sootmass". As expected, soot production was highest in aromatic solvents and low for the "most combustible" species. The data in Table 2 can be interpreted horizontally to show the increase in soot production with decreasing oxygen availability for any species. Viewed vertically, the data show the effect of molecular structure on soot production. Oxygen-containing species show the least amount of soot formation at 5.2 atm, with aromatics producing the most soot. Phenol again shows the effect of intra-molecular oxygen, in this case as a reduction in the amount of soot produced. Aniline also produces less soot than purely hydrocarbon aromatics, though the effect is not as great as for phenol. This suggests that any model of burnrate or soot production must include a correction for the molecular composition of the solvent.

Open-Burn System. The burnrates of seventeen solvents were measured under conditions of varying oxygen content in air supplied at a constant rate. The data are presented in Table 3. The strong effect of oxygen availability observed in the calorimeter studies are similarly apparent in the open-burn results. The average for the fourteen solvents which burned to completion at 15% oxygen was a 33% drop in burnrate, with the effect being largest for the aromatics. The consistency of the trends in the open-burn data and the calorimeter results supports the validity of the furnace design.

Table 2. Soot Formation (expressed as the percent of original mass) Under Conditions of Differing Conditions of Oxygen Availability.

Compound	30.2	Atmospheres of Oxygen			
		20.2	15.2	10.2	5.2
Methanol	0.0	0.0	0.21	0.74	2.03
2-Propanol	0.0	0.0	0.08	0.23	3.93
1-Butanol	0.0	0.0	0.09	0.0	2.02
Ethyl Acetate	0.0	1.36	2.54	1.10	3.29
Vinyl Acetate	0.0	0.0	0.0	0.0	4.32
Butyl Acetate	0.0	0.0	-	0.53	1.82
MEK (1)	0.0	0.11	0.22	0.47	5.53
MIBK (2)	0.0	0.32	0.18	0.34	2.51
Butyraldehyde	0.20	0.12	0.29	0.25	4.75
Acetone	0.0	0.28	0.18	4.09	5.39
Acrylonitrile	0.36	0.29	0.22	0.81	3.31
Hexane	0.0	0.0	0.53	3.57	6.28
Cyclohexane	0.0	0.15	0.43	6.80	4.00
Benzene	0.0	0.0	0.24	6.63	34.1
Toluene	0.17	0.16	0.36	16.2	21.5
Xylenes	0.0	0.25	0.72	7.8	20.6
Aniline	0.0	0.24	1.05	-	16.7
Styrene	0.0	0.0	4.52	10.4	42.1
Phenol	0.0	0.58	0.92	1.83	10.4

1. Methyl Ethyl Ketone.
2. Methyl Isobutyl Ketone.

Table 3. Burnrates (g/min) of Solvents in the Open-Burn System at Different Oxygen Concentrations (air flowrate=10.0 lpm).

Compound	Burnrate, g/min		
	20.0% Oxygen	15.0% Oxygen	10.0% Oxygen
Methanol	0.43	0.42	0.40
2-Propanol	0.30	0.30	NB(1)
1-Butanol(2)	0.26	0.19	NB
Ethyl Acetate	0.42	0.24	NB
Butyl Acetate	0.24	0.23	NB
MFK	0.40	0.30	NB
MIBK	0.25	0.21	NB
Butyraldehyde	0.33	0.24	NB
Acetone	0.57	0.36	NB
Acrylonitrile(2)	0.61	0.35	NB
Hexane	0.55	0.29	NB
Cyclohexane	0.41	0.22	NB
Benzene	0.71	0.38	NB
Toluene	0.40	INC(3)	NB
Xylenes	0.35	INC	NB
Styrene(2)	INC	NB	NB

1. Did Not Ignite.
2. Sample at 35 degrees C.
3. Did Not Burn To Completion.

Prediction of Burnrate and and Soot Production from Physical Properties of the Solvent. Since the introduction of the computer, it has been used as a tool in the acquisition, storage, and retrieval of data. With the recent advances in statistical analysis using computers to handle the matrix mathematics, emphasis has begun to be placed on using the computer to extract information in the data not previously accessible. It is beyond the scope of this paper to introduce the topic of multidimensional analysis; however, the computer programs have been written and experience in the social sciences has demonstrated the utility of "trend analysis" in its broadest sense. For example, using assorted multi-variate analyses, one can detect "trends" in the data which can be used to correlate the data into sets which vary in the same manner. These sets may or may not have any significance, and the possibility of false correlations is large in small datasets such as the one employed in the following discussion. Nevertheless, we applied multivariate analyses (correlation diagrams, rotated factor analysis, linear regression and generalized linearized modelling) to the experimental data a set of physical constants to determine whether a predictive model for burnrate and/or the rate of soot production based on physical properties of the solvent could be obtained. The twenty-four physical constants listed in Table 4 were compiled^{3,4}. Statistical analyses were performed using SAS routines⁵ run on an IBM 370/3033 mainframe computer. Factor analysis was performed in order to group the parameters according to the fundamental property they represent. The pattern was orthogonally (Varimax) rotated and the resulting array matrix was rearranged to the form shown in Table 5. For

Table 4. Physical Constants of Some Commonly-Carried Commodities.

Parameter	Benzene	Toluene	Xylenes	Cyclo- hexane	Hexane
Molecular Weight	78.1	92.1	106.2	84.2	86.2
Melting Point, deg C	5.5	-95.0	-19.6	6.5	97.5
Boiling Point, deg C	80.1	110.6	140.0	80.7	69.0
Density, g/ml	0.8787	0.8660	0.8670	0.7781	0.6600
Refractive Index	1.4691	1.4691	1.4995	1.4266	1.3751
Dielectric Constant	2.28	2.38	2.40	2.03	1.89
Dipole Moment	0.0	0.36	0.31	0.0	0.0
Heat of Vaporization	10254	9368	9904	7830	7627
Heat of Combustion	10012	10154	--	11132	11546
Hildebrand Constant	9.20	8.90	8.76	8.20	7.30
Threshold Limit Value	10	100	100	300	100
Threshold of Smell	5.0	5.0	4.0	0.4	-
Vapor Pressure, mm Hg	76.0	22.0	5.0	78.0	120
Volatility	325	111	29	360	565
Evaporation Factor	3.0	6.1	13.5	-	8.7
Lower Ignition Limit	1.2	1.2	1.0	1.2	1.2
Upper Ignition Limit	8.0	7.0	7.6	8.3	7.4
Flash Point	-11.0	4.4	23.5	-18	-20
Ignition Temperature	555	535	465	260	240
% Carbon	93.3	91.3	90.5	85.6	83.6
% Hydrogen	7.75	8.75	8.75	14.4	16.4
% Oxygen	0.0	0.0	0.0	0.0	0.0
Burnrate, g/min	0.71	0.40	0.35	0.41	0.55
% Sootmass	34.1	21.5	20.6	4.00	6.28

Methanol	2-Propanol	1- Butanol	Acetone	Butyr- aldehyde	Ethyl Acetate
32.0	60.1	74.1	58.1	72.1	88.1
-97.8	-88.5	-90.0	-94.0	-99.0	-83.6
64.7	82.5	117.5	56.5	74.8	77.1
0.7866	0.7808	0.8100	0.7880	0.8016	0.9020
1.3288	1.3776	1.3993	1.3588	1.3843	1.3723
33.6	18.3	17.1	20.7	13.4	6.02
1.70	1.66	1.66	--	--	1.78
9377	10064	10970	7641	--	8301
5417	7899	8628	7366	--	6093
14.5	10.0	13.6	9.78	--	8.88
200	200	50	1000	--	400
5.0	100	25.0	100	--	50
96.0	32.0	4.3	175	--	73
168	105	17	556	--	350
--	--	33.0	2.1	--	2.9
5.5	2.0	1.4	2.5	--	2.1
44.0	12.0	11.3	13.0	--	11.5
12	11.7	37	-18	-6.7	7.2
455	425	340	540	--	460
37.5	60.0	66.0	62.0	--	54.5
2.6	13.4	13.8	10.4	--	9.2
49.9	26.6	22.2	27.6	--	36.3
0.43	0.30	0.26	0.57	0.33	0.42
2.03	3.94	2.02	0.00	4.75	3.29

this interpretation, a value of 0.9 or better was termed significant. The four factors are interpreted on the basis of the parameters which are associated with each, as shown in the table. The first four parameters are strongly correlated with Factor 1, which is interpreted to be a "composition" term. (Refractive index is a measure of the aromaticity of the solvent and is therefore also composition-dependent.) The next set of parameters generally relate to the volatility of the solvent. Volatility appears to relate to both Factors 1 and 2, though more with the latter. The third group of parameters is related to the flammability of the solvent, and correlates with Factor 2. Factor 3, as represented in the fourth group of parameters, is interpreted to be a mass-conversion term. Factor four had no parameters which met the 0.9 significance level.

Burnrates for eleven of the solvents were then added to the matrix, as was the % sootmass at 5.2 atm oxygen (from the calorimeter study). Table 6 shows the correlation coefficients of these two experimental observations with the above parameters. Comparison of Tables 5 and 6 shows that burnrate is most significantly affected by those related to volatility (groups 2 and 3 in Table 5, or Factor 2) whereas burnrate correlated more strongly with composition-dependent parameters (Factor 1). The only parameter to meet the 0.9 correlation level with sootmass, however, was dipole. This serves to illustrate the potential for misleading interpretations due to the small size of the dataset. Since most species were either hydrocarbons (dipole approximately zero) and oxygenated species (eg alcohols, with large dipoles), this parameter acts more like a switch than as a predictor of burnrate. The solvents

Table 5. Rotated Factor Pattern for the Most Significant Parameters

Parameter	Factor 1	Factor 2	Factor 3	Factor 4
Group 1				
Heat of Combustion	-0.99	0.05	-0.05	0.10
% Oxygen	0.98	0.14	-0.09	-0.12
% Carbon	-0.96	-0.20	0.14	0.16
Refractive Index	-.93	0.06	0.36	0.00
Group 2				
Boiling Point	-0.51	0.78	0.23	-0.25
Dielectric Constant	0.47	0.22	0.84	0.16
Dipole Moment	0.55	0.73	0.40	0.08
Volatility	0.48	0.82	-0.26	0.18
Hildebrand Constant	0.05	0.87	-0.48	0.08
Group 3				
Ignition Temperature	-0.32	-0.94	0.05	0.03
Evaporation Factor	-0.06	0.96	-0.27	-0.01
Flash Point	0.04	0.98	0.15	-0.14
Group 4				
Molecular Weight	-0.28	0.15	0.92	-0.20
Density	-0.06	-0.16	0.96	0.22
Group 5				
Melting Point	-0.37	-0.25	0.15	0.88
Heat of Vaporization	-0.57	0.72	0.05	0.39
Threshold Limit Value	0.61	-0.54	-0.51	0.28

Table 6. Correlation Coefficients for Burnrate and % Sootmass with Selected Physical Constants of the Solvent Burned.

Parameter	Correlation Coefficient	
	Burnrate	% Sootmass
Dielectric Constant	-0.73	-0.53
Volatility	0.72	-0.07
Evaporation Factor	-0.72	-0.47
Flash Point	-0.69	-0.15
Vapor Pressure	0.68	-0.18
Upper Ignition Limit	0.67	-0.38
Dipole Moment	-0.65	-0.98
Refractive Index	0.05	0.81
% Hydrogen	0.27	-0.73
% Carbon	-0.27	0.71
Ignition Temperature	0.30	0.65
% Oxygen	-0.23	-0.61
Burnrate	1.00	0.61
Heat of Vaporization	-0.37	0.31
Hildebrand Constant	0.35	0.35
Boiling Point	-0.49	0.35
Heat of Combustion	0.24	0.39
Threshold of Smell	-0.05	0.47
Molecular Weight	-0.04	0.43
Density	-0.04	0.49
Threshold Limiting Value	0.21	-0.59

selected for this discussion are among the most commonly carried rail commodities and represent a wide range of chemical classes (alcohols; aldehydes; aromatics (normal and substituted); cyclic, saturated and unsaturated hydrocarbons). This diversity is partly responsible for the low correlation coefficients obtained. Similar results are obtained for the index of refraction, for example. Without identification of the type of solvent, little correlation is apparent. However, by dividing the data into the respective chemical classes, it may indeed be possible to predict burnrate from a simple set of (e.g. four) physical constants. The present data, however, are too few to permit this for all solvents. Burnrate and sootmass data for several compounds in each chemical class are needed in order to define the trends, and those experiments are underway.

ACKNOWLEDGEMENTS

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MEMBRANE TECHNOLOGY APPLICATIONS
IN ATLANTIC CANADA

H. Whittaker
J. Tremblay

Introduction

The Environmental Emergencies Technology Division (EETD) of the Environmental Protection Service (EPS) was requested, by Atlantic Region of EPS, to bring the mobile reverse osmosis (RO) unit to that region for demonstrations/trials. The objective was to determine and/or demonstrate the applicability of reverse osmosis technology to a landfill which contained PCB's and to the effluent from steel mill coking ovens. Further applications added later included ultrafiltration (UF) of fish plant wastes and RO of potato sludge supernatant and municipal landfill leachate. The trials were carried out in the fall of 1984.

Background

EETD was requested, early in 1984, to bring the mobile RO unit to Nova Scotia to investigate its applicability to two problem areas.

a) The MacDonald Landfill in Amherst:

In 1973 a quantity of waste PCB's were buried at this site. A major excavation was carried out in 1978 but it is estimated that an additional 18,000 kg of PCB's remain. These compounds, which are consolvated with trichlorethylene, are leaching from the landfill.

b) The Sydney Tar Ponds:

An investigation of polynuclear aromatic hydrocarbons in Sydney Harbour has revealed excessive levels with the Sydney Steel Tar Pond as the major source.

Later, when initial planning for the visit was underway, it was requested that the unit also visit:

a) Truro Landfill:

This is an active municipal site which is reputed to have received some hazardous wastes over the years. The leachate from the site enters a stream which flows through an Indian Reserve. The residents of the Reserve have expressed concern that chemicals in the water are affecting their health.

b) Fish Reduction Ltd., Clements Pond, N.S:

This is an industrial process application of U.F. A plant uses coarse fish and fish wastes to produce meal. The liquid residue (fish blood water), which has been finely screened, contains a large amount of protein and fish oil and has a high BOD loading. The only means currently available for disposing of this waste liquid is through shallow injection as a fertilizer.

While detailed planning was underway on Atlantic Region's requests, a request was received from Environment New Brunswick to trial RO on the supernatant from the potato sludge at McCain Foods, Florenceville, N.B. At this location the wastes from raw potato processing, which are acidic, are pumped into a holding pond system where the suspended solids settle out. The supernatant liquid then partially evaporates but some is drained to nearby streams. During periods of low flows in the streams, this can cause too high a BOD loading.

A trip through Nova Scotia and New Brunswick, to accomodate all of these requests, was planned for November, 1984.

Procedure and Results

Potato Sludge Supernatant

This work was funded by Environment New Brunswick. A 180 litre (40 gallon) sample of potato sludge supernatant, containing a larger than normal solids loading and thus representing a worst case situation, was shipped to Memtek Corporation in Nepean, Ontario for preliminary testing. The sample was run on a small RO unit containing four membranes to determine capability of two different membranes to clarify the solution. Testing was carried out at room temperature at a pressure of 5,500 kPa (800 psi). Initial results (Table 1) indicated acceptable flow rates and rejections. It was, therefore, decided to carry out a trial on site using the mobile RO unit.

The mobile unit was configured with two banks of membrane elements, one consisting of 6 Toray SP110 and the other of 6 UOP 1001 (Figure 1). It was towed to a position on the bank of one of the holding ponds and suction was taken directly from the pond. The supernatant was processed for eight hours with periodic taking of samples and readings. Results from this trial are shown in Table 2.

TABLE 1
Reverse Osmosis
Small Scale Testing on Potato Water

<u>Sample</u>	<u>Flux</u>	<u>pH</u>	<u>COD</u>	<u>TOC</u>	<u>SS</u>	<u>TS</u>	<u>TVS</u>
FEED	-	4.3	12800	4150	422	3510	2260
UOP 1	3.1 L/min	3.6	649	184	10	16.5	10
UOP 2	3.3 L/min	3.5	969	316	10	10	10
TORAY 1	2.6 L/min	5.2	221	65.8	10	68	19
TORAY 2	1.0 L/min	4.8	1280	417	10	382	148

All values are in PPM

COD - Chemical oxygen demand
TOC - Total organic carbon
SS - suspended solids
TS - Total solids
TVS - Total volatile solids

TABLE 2

IN SITU TESTING OF REVERSE OSMOSIS ON POTATO WATER

Feed	Flux (l/m)	pH	BOD5	COD	TOC	TS	TVS	NH3-N	K	PO4
P1 (UOP)	-	4.17	8500	11,100	3,300	3560	1710	141	308	110
1.5 HRS	4.1	-	781	1010	486	23.0	22.9	0.79	0.71	0.5
3.5 HRS	3.7	3.5	425	795	363	22.0	10.5	0.5	0.71	0.5
5.5 HRS	4.1	3.5	407	712	339	10	10	.64	0.66	0.5
7.5 HRS	3.7	3.4	414	929	374	13.5	10	0.5	0.54	0.5
P2 (UOP)	4.1	3.5	685	1050	482	19.0	14.0	0.97	1.19	0.5
1.5 HRS	4.1	3.4	562	767	414	12.5	10	0.5	0.89	0.5
3.5 HRS	4.0	3.4	504	910	388	11.0	10	0.73	0.65	0.5
5.5 HRS	4.0	3.5	445	667	326	10	10	0.55	0.59	0.5
P3 (TORAY)	1.5	4.6	728	1230	558	302	139	29.2	64.3	0.5
1.5 HRS	1.3	4.7	590	793	396	249	65	25.2	57	0.5
3.5 HRS	1.3	4.7	457	749	349	221	71.5	18.4	50.0	0.5
5.5 HRS	1.2	4.7	442	703	325	212	90	16.2	49.3	0.5
P4 (TORAY)	2.2	4.9	205	393	186	112	54.5	8.63	21.2	0.5
1.5 HRS	1.2	4.8	251	389	172	110	46.0	16.2	24.4	0.5
3.5 HRS	1.1	4.8	259	353	166	106	46.0	8.9	22.7	0.5
5.5 HRS	1.0	4.8	212	354	154	104	24.5	8.9	24.2	0.5
7.5										

BOD5 - Biological oxygen demand (5 days)
 NH3-N - Kjeldahl Nitrogen
 K - Potassium
 PO4 - Phosphate

Fish Blood Water

The UF membranes used in this trial were funded by EPS Industrial Programs Branch.

The mobile RO unit was configured as a UF unit with 4 parallel UF membrane elements (Figure 2). These were:

- | | | |
|-------------------------|------------------|--------------------|
| a. | DSI U90 G10 | M.W. Cutoff 4000 |
| b. | DSI U90 G20 | M.W. Cutoff 5000 |
| c. | DSI U90 G50 | M.W. Cutoff 15,000 |
| d. | FILMTEC UFP 4040 | M.W. Cutoff 20,000 |
| M.W. - Molecular weight | | |

The unit was placed approximately 5 metres from a large tank containing the blood water. Unfortunately this solution had been stored in the tank for at least three months and had achieved the consistency of a very thick, lumpy porridge which was impossible to either pump or process. A portion was, therefore, diluted with fresh water and transferred to a second tank. Feed for the UF unit was taken directly from the latter tank.

The unit was run for approximately two hours at 1050 kPa (150 psi). The permeate produced was very clear while the concentrate was thick and grey in colour. There was, however, a very rapid decrease in UF permeate flux (flow rate) with time. This was attributed to blinding (plugging of the small pores) of the membrane by fish oil.

The following day the membranes were cleaned, in the unit, with a solution of laundry detergent in lake water and the fluxes returned to near normal levels. The UFP 4040 membrane pressure vessel was disconnected and the unit reconnected to the feed tank. Pressure was set at 2800 kPa (400 psi). Once again it was possible to process the feed solution but again a rapid drop off in the flux occurred. The trial was continued for one hour and then the unit was shut down and the membranes were cleaned. Results of analysis of samples taken during the trial are included in Table 3.

TABLE 3

ANALYSIS OF SAMPLES FROM BLOOD WATER TRIAL (All samples taken at 1030 kPa)

<u>SAMPLE</u>	<u>pH</u>	<u>BOD (PPM)</u>	<u>COD (PPM)</u>	<u>TS (PPM)</u>	<u>TVS (PPM)</u>	<u>SS (PPM)</u>	<u>NH3 (PPM)</u>
FEED	6.6	102000	237500	45200	33600	35600	7560
G10 PERMEATE	6.6	50400	35200	13300	3400	22	9240
G20 PERMEATE	6.6	55000	38100	13300	3200	60	10080
G50 PERMEATE	6.6	53000	35200	13500	3400	45	9800
UFP PERMEATE	6.8	57900	35000	14300	3400	120	13720

Analysis of a sample taken at 2800 kPa (400 psi) revealed a G10 permeate total solids loading of 12,600 ppm.

Sydney Tar Ponds

The work in Sydney was intended to determine the capability of reverse osmosis to remove PAH's from the coking oven effluent water. Unfortunately the coking ovens were not operating during the trial. Tests were, however, carried out at two points:

- a. the main sewer from the coking ovens (Coke Oven Brook); and
- b. the tar ponds. (Figure 3).

The RO unit was configured as per the potato water work. It was first run at the Coke Oven Brook location, on very dirty water. The trial was carried out for 6 hours at a 1:1 concentrate/permeate ratio with samples being taken and flow rates being measured every hour. Flux rates are shown in Table 4. Preliminary analysis of samples has failed to detect PAH's in the feed or permeates.

TABLE 4

CONCENTRATE AND PERMEATE FLUXES - COKE OVEN BROOK

<u>TIME (HOURS)</u>	<u>CONCENTRATE (L/M)</u>	<u>PERMEATE L/M</u>
00	28	31
02	23	24
04	22	22
06	21	21

The last UOP permeate sample appeared dirty (all of the others had been clear). Investigation the next day showed that at least one of the UOP membrane elements had begun to telescope.

The trial at the tar pond was of only a very short duration. This was necessitated by the leaking membrane and by the presence of bacterial growth noticed in some membranes during the investigation. The latter problem,, which was probably the result of the potato water work, was cured by flushing with 5 percent formaldehyde solution.

Truro Municipal Landfill

The work at this location was intended to concentrate the chemicals in the landfill leachate in order to detect any which might be harmful. Normally concentration by a factor of 20, of larger molecules, is relatively easy for the mobile RO unit. In this instance, however, the leaking UOP membrane element prevented any high concentrations being achieved. Samples were taken, none-the-less and analysed for TOC, PCB's and total chlorinated organics (TCO). The results of the analysis are shown in Table 5.

TABLE 5ANALYSIS OF TRURO LANDFILL LEACHATE

<u>SAMPLE</u>	<u>PCB (PPB)</u>	<u>TOC (PPM)</u>	<u>TCO (PPM)</u>
FEED - 6.0 HRS	NID	240	NOT MEASURED
TORAY PERMEATE - 6.0 HRS	NID	21	NOT MEASURED
CONCENTRATE - 0.0 HRS	0.25	800	NOT MEASURED
CONCENTRATE - 2.0 HRS	TRACE	760	0.3 as Cl

Amherst (MacDonald Landfill)

The objective at this location was to determine the capability of reverse osmosis to remove the high levels of PCB's reported to be present in the leachate. (The PCB level in the leachate had been reported to exceed 1-2 ppm, far above the normal solubility of PCB's because of the consolvation effect of the trichlorethylene). A hole which had been dug in the landfill contained approximately 20,000 litres of leachate. This was used as feed for the mobile RO unit, at 1:1 concentration ratios during a 4 hour trial. Samples were taken from the Toray permeate, the feed and concentrate. Results of analysis of these samples are reported in Table 6.

TABLE 6ANALYSIS OF MACDONALD LANDFILL LEACHATE

<u>SAMPLE</u>	<u>PCB (PPB)</u>	<u>TOC (PPM)</u>
FEED 0.0 HRS	3.5	50
CONCENTRATE 0.0 HRS	1.5	110
CONCENTRATE 4.0 HRS	3.4	135
TORAY PERMEATE 0.0 HRS	N/D	1.0
TORAY PERMEATE 1.5 HRS	N/D	2.0
TORAY PERMEATE 3.0 HRS	N/D	36.0

On completion of the work at Amherst, the unit was flushed with permeate and returned to Ottawa.

Discussion of ResultsPotato Sludge Supernatant

The analytical results in Table 1 show the very high separation achieved during the small scale testing. These varied from 80 percent to greater than 99.7 percent. The membrane element which produced the lower figure had previously been used 180 hours on the cleanup of a wood preservative spill and was probably damaged somewhat. The fact that it had a very low flux emphasizes that it was probably damaged internally.

The in situ results indicate that the UOP 1001 membranes are superior to the Toray, at least in the short term. The difference between P3 and P4 may indicate that one of the membranes in that pressure vessel was damaged during a 44 hour processing of PCB leachate which was carried out earlier.

Fish Blood Water

The very rapid decrease in permeate flux observed during the testing was most probably the result of "blinding" of the membrane by the fish oils present in the feed. The feed was, in this instance, at least three months old and had changed greatly from its original condition. It was not known if the same results would be achieved with a fresh feed solution but, if this was the case, then spiral wound UF membrane elements are not appropriate for this purpose. Tubular UF membrane elements should be tried instead.

BOD, COD and SS reductions of the order of 50 percent, 85 percent and 99 percent were achieved in the permeates. Similar reductions are probably achievable with tubular membranes. If the permeate levels shown in Table 3 are too high for discharge, the use of reverse osmosis on the UF permeate should be considered.

Sydney Tar Ponds

It is unfortunate that the coking ovens were not in operation during this trial. The result is that the original purpose of that particular trial, to determine the ability of reverse osmosis to remove PAH's from the stream was not possible. The telescoping which occurred with at least one of the UOP 1001 RO membrane elements indicates that these membranes may not be suitable for that purpose. It is noted that the Toray membranes, which had previously been used for 710 hours on dilute chemical leachate and 44 hours on PCB contaminated leachate do not seem to have been affected.

Truro Municipal Landfill

The purpose of this trial was to concentrate any chemical known to be deleterious to the health for ease of analysis. It appears that PCB's may be present but with a concentration of less than 50 ppt. Total chlorinated organics, measured as Chlorine shows a level of 0.3 ppm indicating the presence of chlorinated organics other than PCB's in the leachate.

MacDonald Landfill (Amherst N.S.)

It is obvious from Table 6 that the ppm levels of PCB's previously reported were not present in the water in the dug hole which was used for feed. This does not mean, however, that these levels are not present in other areas of the landfill.

The apparent reduction in PCB's between the feed and the concentrate indicates that either the PCB's are attached to suspended solids in the leachate and were removed by the 25 micron pre-filters or that they were present in conjunction with another chemical which separated from solution and did not appear in the aqueous phase of the concentrate.

Conclusions

The work which was carried out by the mobile RO/UF unit in Atlantic Canada is considered to have been very useful. On the basis of the data obtained it is concluded that:

- a. Reverse osmosis may be a viable option for preventing environmental contamination caused by potato sludge supernatant. Further studies would be required to determine the applicability of this technology in the longer term;
- b. Although ultrafiltration is effective for removing much of the solids loading from fish blood water, the spiral wound membranes used are not suitable for that purpose. Tubular UF membranes should probably be tried;
- c. the capability of RO to remove PAH's from the tar ponds' water has not been determined. It is, however, suspected that the UOP 1001 membrane is not suitable for that purpose;
- d. the level of PCB's in the leachate from the Truro landfill is less than 50 ppt. They do, however, appear to be present in smaller quantities; and,
- e. reverse osmosis is effective in removing the PCB's from the MacDonald landfill leachate at least at the levels found in the test hole.

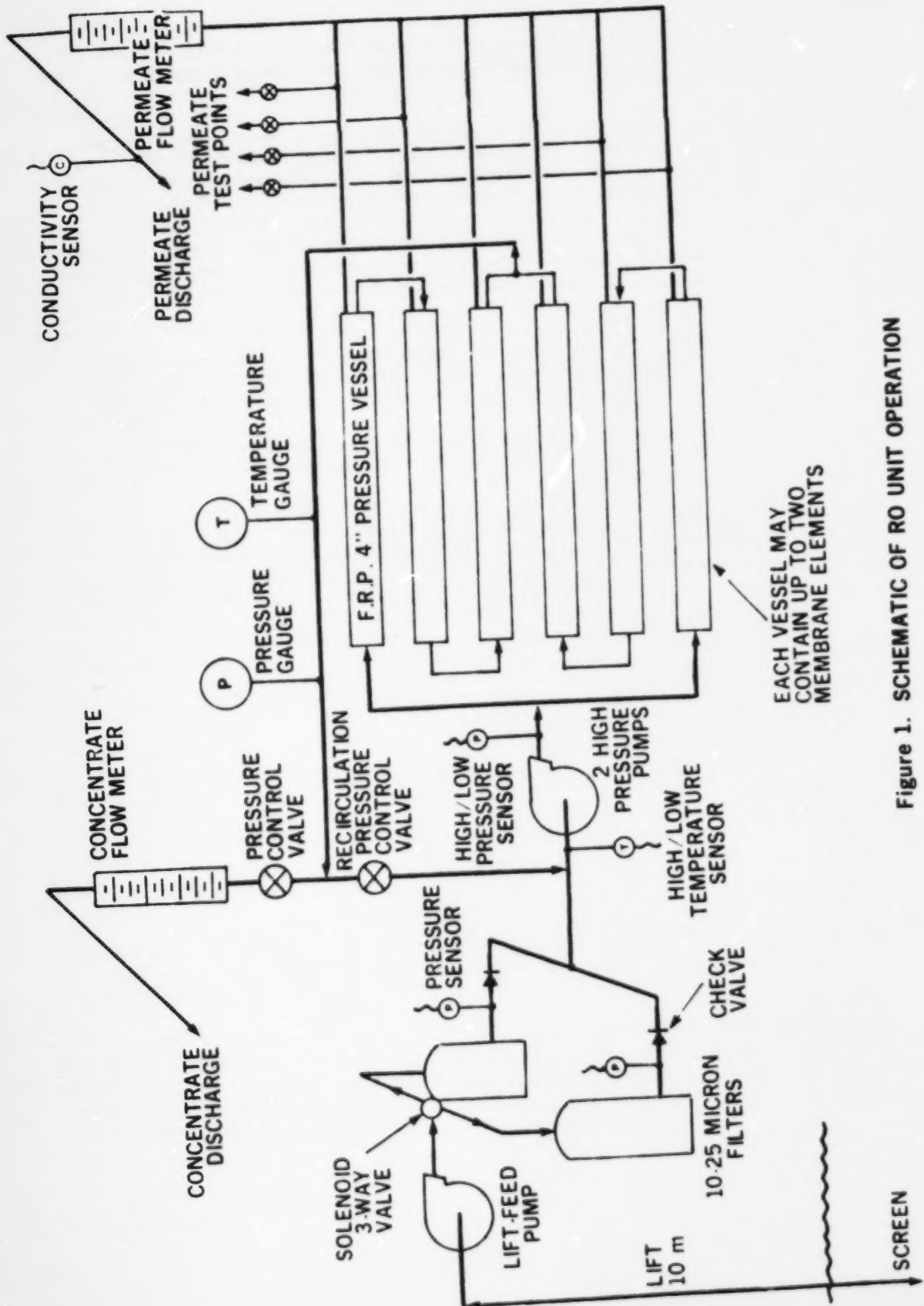


Figure 1. SCHEMATIC OF RO UNIT OPERATION

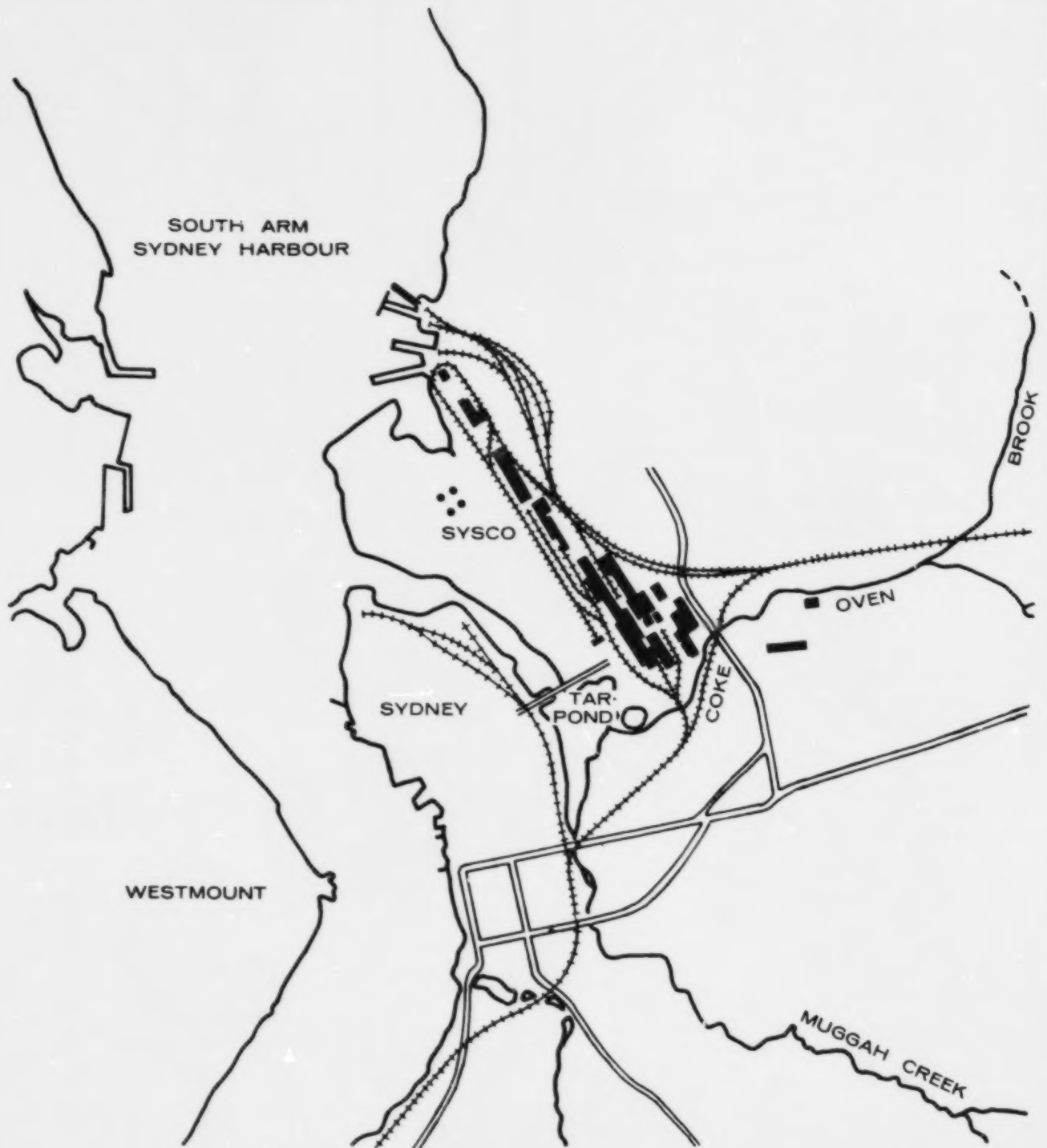


Figure 3. SYDNEY TAR POND LOCATIONS

TESTING OF REVERSE OSMOSIS
ON CHEMICAL SOLUTIONS

H. Whittaker	EETD
T. Szaplanczay	Memtek

Introduction

A mobile reverse osmosis (RO) unit has been built for Environment Canada. It is a dual purpose machine, capable of either producing fresh water for oil spill cleanup or concentrating aqueous solutions from a chemical spill, leachate or industrial effluent.

The heart of the RO unit is the membrane. Products from four different manufacturers were purchased and evaluated on a series of pure chemical solutions. Varying results were achieved but the promise of RO as a technique for concentration was proven.

Background

A mobile reverse osmosis (RO) unit has been manufactured for the Environmental Protection Service (EPS) of Environment Canada. (1) The unit, is designed for two purposes:

- a) to provide fresh water from salt water for steam cleaning of rocky shorelines in remote areas; and
- b) to concentrate dilute aqueous chemical solutions resulting from spills into small bodies of freshwater.

It also has potential as a means of determining the applicability of reverse osmosis to various industrial effluents.

The unit, which is completely self-contained, is capable of producing from 1800 to 2400 litres per hour of potable water from sea water depending on the membrane used. Its capacity for chemical spill cleanup varies, similarly, with the membrane used and with the concentration and identity of the chemical. It was, therefore, decided to determine the applicability of the concept by carrying out a series of tests using frequently spilled chemicals and commercially available membranes.

Letters were sent to all known membrane manufacturers and their Canadian distributors. The letter contained an explanation of the purpose of the trial and the list of chemicals from which those to be used during the test would be chosen. The manufacturers were requested to provide information concerning any testing which they had carried out on those or similar chemicals and to recommend one of their membranes for the test program. Based on the responses received, the following membranes were chosen:

- a) TORAY PEC 1000 SP110;
- b) UOP TFC 4600;
- c) FILMTEC FT 30; and
- d) DSI B441.

The chemicals chosen were from a list of commonly spilled hazardous chemicals developed by EETD. The chemicals chosen, which are considered to be very representative, were based on the principle that the ability of reverse osmosis to remove a chemical from aqueous solution is highly dependent upon the size of the molecule and the functional group. Within a given functional group (e.g. alcohol, acid, alkali, ketone), the smaller the molecule, the more difficult it is to remove. Those chemicals chosen are included in Table 1; the last member of the list, which is not a commonly spilled chemical, was included at the request of Canadian National Railways who had had a spill of that chemical into the soil on a rail right-of-way.

Methodology

The test program was carried out under contract by Memtek Corporation of Nepean Ontario and by Miss Aileen Larkin of Waterloo University. Analyses of the samples was done by Miss Larkin and Mr. Gerard Tessier.

Reverse Osmosis Testing

The mobile reverse osmosis unit used in this project can accommodate up to twelve (12) 10 cm (4 in) diameter, 100 cm (40 in) long elements in six fiberglass pressure tubes. (Figure 1) In these tests, only four membrane elements and consequently four pressure tubes were used. The plumbing of the unit was modified to provide sample ports to each of the four permeate lines for permeate flow (flux) rate determination, and for taking representative samples. (Figure 2).

Water Used in the Tests

In all the tests carried out during this project, purified water (produced by a separate RO unit employing cellulose acetate membranes) was used exclusively, using Ottawa City water as feed. The reason for this was twofold: to eliminate the chlorine in the City water, which could be harmful to the TFC membranes, and to eliminate approximately 95 percent of the various elements present in the City water.

Flushing the Mobile Unit

Before the project started, the mobile unit was flushed with approximately 5600 litres of purified water, and both permeate and concentrate were discarded. The flushing removed any preservatives or other chemical compounds which may have been present in the new membrane modules.

Base Line Test

Following the flushing of the mobile unit a "base line" test was carried out. This consisted of the following steps:

Approximately 1900 litres of permeate was produced from Ottawa city water and stored in a polypropylene tank.

The mobile unit was started, and using the above permeate as feed, the pressure was adjusted to 4100 kPa (600 psi) and the permeate/concentrate ratio to 2:1. Both concentrate and permeate produced by the mobile unit were discarded. After approximately 15 minutes of operation (steady state) 2.5 litres of permeate was collected from each of the four sample ports (four membranes), the times required were measured by a stopwatch, and the temperature of the feed water was recorded. From these data the flux rates of the four membranes could be calculated. The above procedure was repeated at 4:1 and 8:1 permeate/concentrate ratios, without interruption.

This "base line" test was repeated after each chemical solution test.

The reasons for these "base line" tests were the following: to flush the mobile unit after each chemical test to prevent cross contamination, and to indicate if fouling (low flux rate) or rupture (high flux rate) had occurred.

Preparation of Chemical Solutions

In approximately 1900 litres of permeate (polypropylene tank), a sufficient amount of the chemical compound was dissolved to give the desired concentration. The concentration of the chemical solutions varied from 10 to 1000 ppm. A hand held mixer with a 1.4 metre (4.5 ft) shaft was used for the mixing.

Chemical Test Procedure

After the chemical solution had been prepared, the mobile unit was started using the solution in the tank as feed. The pressure was adjusted to 4100 kPa, the permeate/concentrate ratio 2:1 and both concentrate and permeate were returned to the tank (recirculated). After approximately one half hour of recirculation the flux rates of the membranes were measured. At the same time samples were taken for chemical analyses of the permeates, the concentrate and feed. The above procedure was repeated at 4:1 and 8:1 permeate/concentrate ratios without interruption.

When the test was completed, the mobile unit was turned off, the solution from the tank was drained using a pump and the tank was cleaned and rinsed. Approximately 1900 litres of permeate was prepared into a clean tank and "base line" test was carried out to clean the mobile unit and check the flux rates of the membranes.

Order of Testing of Chemicals

The chemicals were used in the tests in the order given below:

- 1) Acetic Acid
- 2) Ammonium nitrate
- 3) Zinc sulphate
- 4) Potassium hydroxide
- 5) Urea
- 6) (sodium chloride)
- 7) Formaldehyde

- 8) Ethylene dichloride
- 9) Propylene oxide
- 10) Methanol
- 11) Benzene
- 12) 2,4,-D
- 13) Parachlorobenzotrifluoride
- 14) Ferric chloride
- 15) Hydrofluoric acid
- 16) Calcium phosphate (dibasic)
- 17) Sodium chlorate
- 18) (sodium choride)

The above order of chemical was selected to complete the least troublesome chemical test first, and leave the expected troublesome ones to the end. It was anticipated that the ferric chloride and calcium phosphate would foul the membranes and that the sodium chlorate could damage the membranes. The sodium chloride tests were carried out to check the rejection of the membranes after those tests.

Cleaning of the Membranes

There were only two occasions when more than the routine flushing during "base line" determination was needed to restore the flux rates of some of the membranes.

The first cleaning was necessary after the 2,4,-D test, when approximately 0.8 volume percent ethyl alcohol was recirculated in the system for 20 minutes, and the second after the ferric chloride test, when hydrochloric acid (pH = 1.75) was recirculated for 20 minutes. The temperature of these cleaning solutions was ambient.

Calculation of the Flux Rates

2.5 litres of permeate was collected for the flux rate determinations, the time required and the temperature of the feed being recorded at the same time. The flux rate valued reported in Table 2 and Figures 3 to 6 are converted to litres per minute at 25°C (77°F), and are the averages of three determinations i.e. at 2:1, 4:1 and 8:1 permeate/concentrate ratios.

The standard deviations of these averages rarely exceeded 5 percent relative (max 10 percent), and were usually in the 1 percent to 2.5 percent range, indicating the good reproductibility of the tests.

Sodium Chloride (rejection) Tests

A rejection test was carried out after the urea test because the flux rates of TORAY, UOP and Desalination membranes increased by approximately 30 percent. It was suggested that the potassium hydroxide test, carried out prior to the urea test, might have damaged the membranes. The results, given below, indicated that no damage to the membrane had occurred. The conditions were: approximately 2000 ppm NaCl, 4100 kPa (600 psi), permeate/concentrate ratio 4:1, ambient temperature.

<u>Manufacturer</u>	<u>Rejection %</u>
TORAY	99.8
UOP	95.5
Desalination Systems	98.3
Filmtec Inc.	98.0

The rejection test was repeated after the last chemical test (sodium chlorate) under the same conditions, and the results (reported below) indicated no appreciable difference in rejection, compared to the first test.

<u>Manufacturer</u>	<u>Rejection</u>
TORAY	99.8
UOP	96.3
Desalination	97.0
Filmtec Inc.	97.8

Although it could be concluded that the chemicals tested did not damage the membranes, it is not possible due to the comparatively short duration of the tests, to predict the expected life of the membranes.

Analyses of Samples

Analyses of concentrate, feed and permeates were carried out as follows:

- a) ultraviolet spectrometry
 - (i) acetic acid
 - (ii) benzene
 - (iii) ethylene dichloride
 - (iv) urea
 - (v) propylene oxide
 - (vi) 2,4,-D
 - (vii) parachlorobenzotrifluoride
 - (viii) sodium chlorate
- b) specific ion electrode
 - (i) ammonium nitrate
 - (ii) hydrofluoric acid
- c) pH meter
 - (i) potassium hydroxide
- d) gas chromatography - purge and trap
 - (i) formaldehyde
- e) atomic absorption spectroscopy
 - (i) zinc sulphate
 - (ii) ferric chloride
 - (iii) calcium phosphate

An attempt was made to determine methanol concentrations by the GC Purge and Trap method. It was unsuccessful because of the problems encountered in attempting to obtain accurate dilutions down to the unsaturated range of the detector.

Ultraviolet Spectrometry

UV determinations were carried out on a Perkin-Elmer 522A UV/VIS Spectrophotometer using matched quartz cuvettes. The methodology used was as follows:

- a) a standard solution of the chemical was made up at approximately 10 times the concentration in the feed;
- b) the standard was run on the UV spectrophotometer to determine location of peaks;
- c) successive dilutions of the standard were made up to determine the concentration range for the chemical in which the linear Beer's Law applied;
- d) a curve of concentration vs absorbance was made up for the linear region;
- e) the samples from the RO unit were diluted as necessary to fall within the linear region; and
- f) concentration was established from the standard curve.

Specific Ion Electrode

Measurements of specific ion concentration were made using Orion Research specific ion electrodes and a Fisher Model 825 MP pH Meter. This was accomplished in the following manner:

- a) a standard solution of known concentration was used to prepare a series of solutions, spanning the expected range of concentrations;
- b) a standard curve of concentrations vs millvolt conductance was produced and the linear region determined;
- c) RO samples were diluted to lie within the linear range and then run; and
- d) concentrations were determined from the standard curve.

pH Meter

The same procedure and equipment was used as for the specific ion electrode determinations. A pH electrode was used in lieu of a specific ion electrode.

Gas Chromatography - Purge and Trap

This procedure was carried out on a Hewlett Packard Model 5830 Gas Chromatograph using a Model 7675A Purge and Trap Unit and an FID. A 5 ml aqueous sample was used, the procedure being as follows:

- a) a 5000 ppm solution of formaldehyde was made up and aliquots of this solution were diluted to make 1000, 100, 10 and 1 ppm solutions;
- b) the solutions were used to prepare a calibration curve; and
- c) the RO samples were run and their concentrations determined from the calibration curve.

Atomic Absorption Spectroscopy

The analyses were carried out using a Perkin Elmer Model 460 Atomic Absorption Spectrophotometer as follows:

- a) standard samples of solution containing the cation to be determined were made up in concentrations where linearity of response could be assured;
- b) a calibration curve was prepared; and
- c) the RO samples were diluted as necessary until their response on the AA fell within the linear unit and the concentration of the initial solution was determined.

Results

Flux Rates

The flux rates achieved for the four membranes tested are tabulated in Table 2 and Figures 3 to 6. As discussed earlier, these data are the average of those achieved during the runs at 2:1, 4:1 and 8:1 concentration ratios. The numbers shown are not those recorded but are those which would have been achieved at 25°C, the standard temperature for reporting RO membranes results. Actual water temperatures during the runs were within a few degrees of 10°C.

Rejections

The rejections achieved by the four membranes tested are tabulated in Tables 3 to 5. This data is for 4100 kPa (600 psi) at the ambient water temperature.

Rejection percentages are based on the calculation:

$$1 - \frac{\text{Concentration in Permeate}}{\text{Concentration in Feed}} \times 100$$

Discussion of Results

Flux Rates

Figure 3 Toray Membrane

The "base line" flux rate of the Toray membrane increased by approximately 50 percent during the eighteen tests. The flux rate increased gradually except after test no. 14, (ferric chloride followed by hydrochloric acid cleaning) when the flux rate increased substantially. This high flux rate was maintained during test no. 15 (hydrochloric acid), and declined somewhat during the subsequent tests. It would thus appear that from relative flux rate point of view the Toray membrane seems to be a poor choice for strong base separation (test no. 4) while a good choice for acid separation (test no. 1, 14, 15). The other interesting observation is that the Toray membrane seems to be the least affected by solids in the feed (test no. 12, 14) in agreement with the manufacturer's claim.

It should also be noted that the flux rate of the Toray membrane is equal to or less than 50 percent of the other three membrane's flux rates.

Figure 4 UOP Membrane

The "base line" flux rate of the UOP membrane increased by approximately 35 percent during the eighteen tests. The largest increases in flux rates occurred after the strong base (test no. 4) and the acid tests (test no. 14, 15). From the flux rate point of view the UOP membrane seems to be a good choice for both basic and acidic solution separations, but it is affected by suspended solids (test no. 12, 14). Proper cleaning would restore the flux rates.

Figure 5 Desalination Membrane

The Desalination membrane showed the largest increase in "base line" flux rate at approximately 60 percent. The increase in "base line" flux rate occurred after the strong base (test no. 4) and the acidic tests (test no. 14, 15). From flux rate point of view, the Desalination membrane seems to be a poor choice for basic solutions, a good choice for acid solutions, and seems to be fairly tolerant for suspended solids or precipitates (test no. 12, 14). The Desalination membrane had the highest final flux rate.

Figure 6 Filmtec Membrane

There was no change in the Filmtec membrane's "base line" flux rate at the end of the eighteen tests as compared to the first "base line" test. The graph shows that the product flux rate is greatly affected by suspended solids or precipitates (test no. 12, 14), but the flux rate could be restored by proper cleaning.

Rejections

The data for the rejections at the various concentration ratios are included in Tables 3 to 5. This data is for the conditions used during the test; 4100 kPa (600 psi) and approximately 10°C feed water temperature. A higher pressure could not be used because of the pressure limitation of the UOP FTC 4600 membrane element. Later work has revealed that higher rejections and flux rates are achieved for the Toray, Filmtec and DSI membranes at their designed operating pressure of 5500 kPa (800 psi).

The tabulated data for calcium phosphate appear to be in error. All of these membranes should reject in excess of 95 percent of the calcium ions at these concentrations and, in other testing, this was achieved. It is suspected that an error occurred during analysis.

The Toray membrane consistently had the highest rejection; 13/15 at 2:1, 12/15 at 4:1, and 14/15 at 8:1. This membrane also showed the lowest decrease in rejection with increasing concentration ratio.

The DSI membrane usually had the second best rejection. It did, however show a marked decrease in rejection with increasing concentration ratio for many of the chemicals.

The Filmtec membrane was slightly superior to the UOP TFC 4600. It should, however, be noted that the former was operated at much lower than optimum pressures while the latter was at its design limit. In later testing, the Filmtec membrane showed a marked increase in rejection, at least for large molecules, at its optimum operating pressure.

As explained earlier, the rejection of a chemical in RO tends, within the same functional group, tends to be higher for the larger molecules (eg. butanol propanol ethanol methanol). It is, therefore, expected that better rejections would be achieved, for all of the membranes tested, if the solution contained larger and more complex molecules. This is shown, at least in part, by the very high rejection of 2,4 D (2,4 - dichlorophenoxy acetic acid) relative to acetic acid for all of the membranes tested.

General

The concentrations chosen for this trial were, where possible, considered representative of what would be found in an actual spill. Rejections and flux rates achieved are, given the constraints mentioned in the Discussion section, considered representative of the "real world".

The best membrane tested, from the rejection stand point, Toray had the lowest flux. This is the dilemma that the person employing reverse osmosis in an actual spill cleanup or industrial discharge would face. Does he choose a high flux rate and accept lower rejections or does he choose a high rejection and an increased time required for the cleanup or more membranes. The choice would probably be based primarily on the degree of cleanliness in the discharge permeate which authorities required.

Conclusions

It is concluded that reverse osmosis can be used successfully to remove many commonly spilled chemicals from aqueous solution. As such, it could be an important tool in the arsenal of pollution prevention measures. It must, however, be emphasized that the results achieved in this trial are for the short term only. Changes may occur in a longer trial.

TABLE 1

Reverse Osmosis Testing-Chemical Selection

<u>Functional Group</u>	<u>Chemical</u>	<u>Solubility</u>	<u>Solution Strength</u>
Organic Acid	Acetic Acid		480 ppm
Inorganic Acid	Hydrofluoric Acid		385 ppm
Alkali	Potassium Hydroxide	1,070,000 ppm	900 ppm
Aromatic	Benzene	1,800 ppm	1000 ppm
Organic Oxide/Ether	Propylene Oxide	65,000 ppm	1000 ppm
Organic Chloride	Ethylene Dichloride	8,700 ppm	1160 ppm
Inorganic Chloride	Ferric Chloride	744,000 ppm	190 ppm
Aldehyde/Ketone	Formaldehyde		790 ppm
Amide	Urea	780,000 ppm	760 ppm
Inorganic Nitrate	Ammonium Nitrate	1,920,000 ppm	140 ppm
Inorganic Phosphate	Calcium Phosphate	300 ppm	10 ppm
Inorganic Sulphate	Zinc Sulphate	965,000 ppm	260 ppm
Chlorate	Sodium Chlorate	1,010,000 ppm	800 ppm
Pesticide	2,4,-D	900 ppm	220 ppm
Dye intermediate	p-Chlorobenzotrifluoride	50 ppm	4 ppm

Note: Methanol was included in the test program but proved impossible to analyse using available equipment.

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TABLE 2

PERMEATE FLOW RATES (FLUX) - Litres/Minute at 25°C

	TORAY		UOP		DESAL.		FILMTEC	
Base Line (B.L.)	2.57	-	6.55	-	6.06	-	8.25	-
Acetic Acid	-	3.07	-	5.11	-	7.08	-	7.27
B.L.	2.95	-	6.17	-	6.74	-	8.06	-
Ammonium Nitrate	-	3.26	-	5.75	-	7.91	-	7.23
Zinc Sulphate	-	2.38	-	5.79	-	4.73	-	4.16
B.L.	2.50	-	6.85	-	5.45	-	7.65	-
Potassium Hydroxide	-	0.83	-	7.12	-	4.39	-	6.02
B.L.	3.33	-	9.08	-	8.25	-	7.84	-
Urea	-	2.54	-	8.40	-	7.04	-	7.25
B.L.	2.57	-	8.63	-	7.57	-	7.57	-
Sodium Chloride	-	2.84	-	6.40	-	7.57	-	5.07
B.L.	3.22	-	8.52	-	8.52	-	7.76	-
Formaldehyde	-	2.95	-	8.06	-	7.65	-	5.60
B.L.	2.99	-	8.48	-	8.21	-	7.65	-
Ethylene Dichloride	-	2.69	-	7.57	-	6.74	-	6.28
B.L.	2.95	-	8.40	-	7.99	-	7.50	-
Propylene Oxide	-	2.95	-	8.37	-	7.57	-	7.19
B.L.	3.10	-	8.44	-	8.25	-	7.61	-
Methanol	-	3.14	-	8.52	-	8.33	-	7.87
B.L.	3.22	-	8.59	-	8.59	-	7.91	-
Benzene	-	3.14	-	8.06	-	7.91	-	7.19
B.L.	3.10	-	8.18	-	2.14	-	7.65	-
2,4,-D	-	3.29	-	1.55	-	5.22	-	1.74
B.L.	3.86	-	4.73	-	8.44	-	5.72	-
B.L. after cleaning	3.71	-	7.19	-	2.30	-	7.68	-
Parachlorobenz. Trifluor.	-	3.56	-	7.46	-	8.29	-	7.31
B.L.	3.56	-	7.50	-	8.59	-	7.65	-
Ferric Chloride	-	3.97	-	6.83	-	6.51	-	3.67
B.L. after cleaning	4.62	-	6.97	-	8.63	-	5.68	-
Hydrofluoric Acid	-	5.15	-	7.91	-	10.18	-	6.09
B.L.	4.69	-	8.86	-	2.87	-	8.44	-
Calcium Phosphate (dibasic)	-	3.57	-	8.25	-	9.54	-	7.61
B.L.	4.09	-	8.86	-	10.86	-	8.48	-
Sodium Chlorate	-	4.13	-	8.03	-	9.58	-	7.08
B.L.	4.05	-	8.90	-	9.77	-	8.25	-
Sodium Chloride	-	4.28	-	8.14	-	9.73	-	6.66

TABLE 3

REVERSE OSMOSIS TESTING RESULTS - MEMBRANE SEPARATION EFFICIENCIES

2:1 concentration ratio 4100 kPa (600 psi)

<u>Chemical</u>	<u>Toray PEC 1000</u>	<u>UOP TFC 4600</u>	<u>Film TEC FT30</u>	<u>DSI B441</u>
Acetic Acid (470 ppm)	72%	51%	34%	64%
Hydrofluoric Acid (400 ppm)	18%	15%	23%	20%
Potassium Hydroxide (900 ppm)	83%	79%	11%	75%
Benzene (1000 ppm)	99%	9%	45%	98%
Propylene Oxide (1000 ppm)	70%	37%	39%	64%
Ethylene Dichloride (1180 ppm)	93%	8%	83%	64%
Ferric Chloride (520 ppm)	99%	99%	99%	97%
Formaldehyde (710 ppm)	95%	34%	64%	80%
Urea (790 ppm)	76%	20%	20%	47%
Ammonium Nitrate (680 ppm)	99%	92%	86%	97%
Calcium Phosphate (10 ppm)	38%	49%	28%	43%
Zinc Sulphate (670 ppm)	98%	98%	95%	98%
Sodium Chlorate (900 ppm)	99%	87%	93%	99%
2,4-D (220 ppm)	99%	86%	97%	95%
p-chlorobenzotrifluoride (5 ppm)	99.5%	98%	82%	88%

Concentration Ratio is the ratio of $\frac{\text{Permeate Flux}}{\text{Concentrate Flux}}$

TABLE 4

REVERSE OSMOSIS TESTING RESULTS - MEMBRANE SEPARATION EFFICIENCIES

4:1 concentration ratio 4100 kPa (600 psi)

Chemical	Toray PEC 1000	UOP TFC 4600	Film TEC FT30	DS1 B441
Acetic Acid (480 ppm)	67%	44%	25%	64%
Hydrofluoric Acid (400 ppm)	20%	13%	16%	16%
Potassium Hydroxide (900 ppm)	81%	51%	3%	73%
Benzene (1000 ppm)	99%	(-9%)	27%	80%
Propylene Oxide (1000 ppm)	47%	32%	30%	50%
Ethylene Dichloride (1160 ppm)	52%	(-14%)	86%	48%
Ferric Chloride (550 ppm)	99%	99%	98%	97%
Formaldehyde (790 ppm)	93%	12%	53%	68%
Urea (760 ppm)	66%	(-2%)	25%	3%
Ammonium Nitrate (790 ppm)	99%	90%	82%	95%
Calcium Phosphate (10 ppm)	43%	45%	44%	41%
Zinc Sulphate (640 ppm)	98%	90%	96%	98%
Sodium Chlorate (800 ppm)	99%	83%	91%	88%
2,4-D (220 ppm)	99%	84%	97%	95%
p-chlorobenzotrifluoride (4 ppm)	99%	98%	77%	84%

Concentration Ratio is the ratio of Permeate Flux
Concentrate Flux

TABLE 5

REVERSE OSMOSIS TESTING RESULTS - MEMBRANE SEPARATION EFFICIENCIES

8:1 concentration ratio 4100 kPa (600 psi)

Chemical	Toray PEC 1000	UOP TFC 4600	Film TEC FT30	DSI B441
Acetic Acid (450 ppm)	60%	31%	11%	47%
Hydrofluoric Acid (400 ppm)	17%	12%	16%	16%
Potassium Hydroxide (950 ppm)	79%	45%	(-8%)	53%
Benzene (1000 ppm)	99%	(-27%)	18%	79%
Propylene Oxide (1000 ppm)	70%	28%	28%	55%
Ethylene Dichloride (1260 ppm)	83%	(-16%)	14%	62%
Ferric Chloride (520 ppm)	99%	99%	98%	96%
Formaldehyde (770 ppm)	93%	8%	43%	67%
Urea (730 ppm)	63%	(-3%)	0	22%
Ammonium Nitrate (680 ppm)	97%	82%	68%	91%
Calcium Phosphate (5 ppm)	22%	31%	27%	18%
Zinc Sulphate (670 ppm)	98%	89%	96%	94%
Sodium Chlorate (800 ppm)	98%	73%	89%	83%
2,4-D (210 ppm)	99%	83%	96%	75%
p-chlorobenzotrifluoride (4 ppm)	99%	95%	81%	74%

Concentration Ratio is the ratio of $\frac{\text{Permeate Flux}}{\text{Concentrate Flux}}$

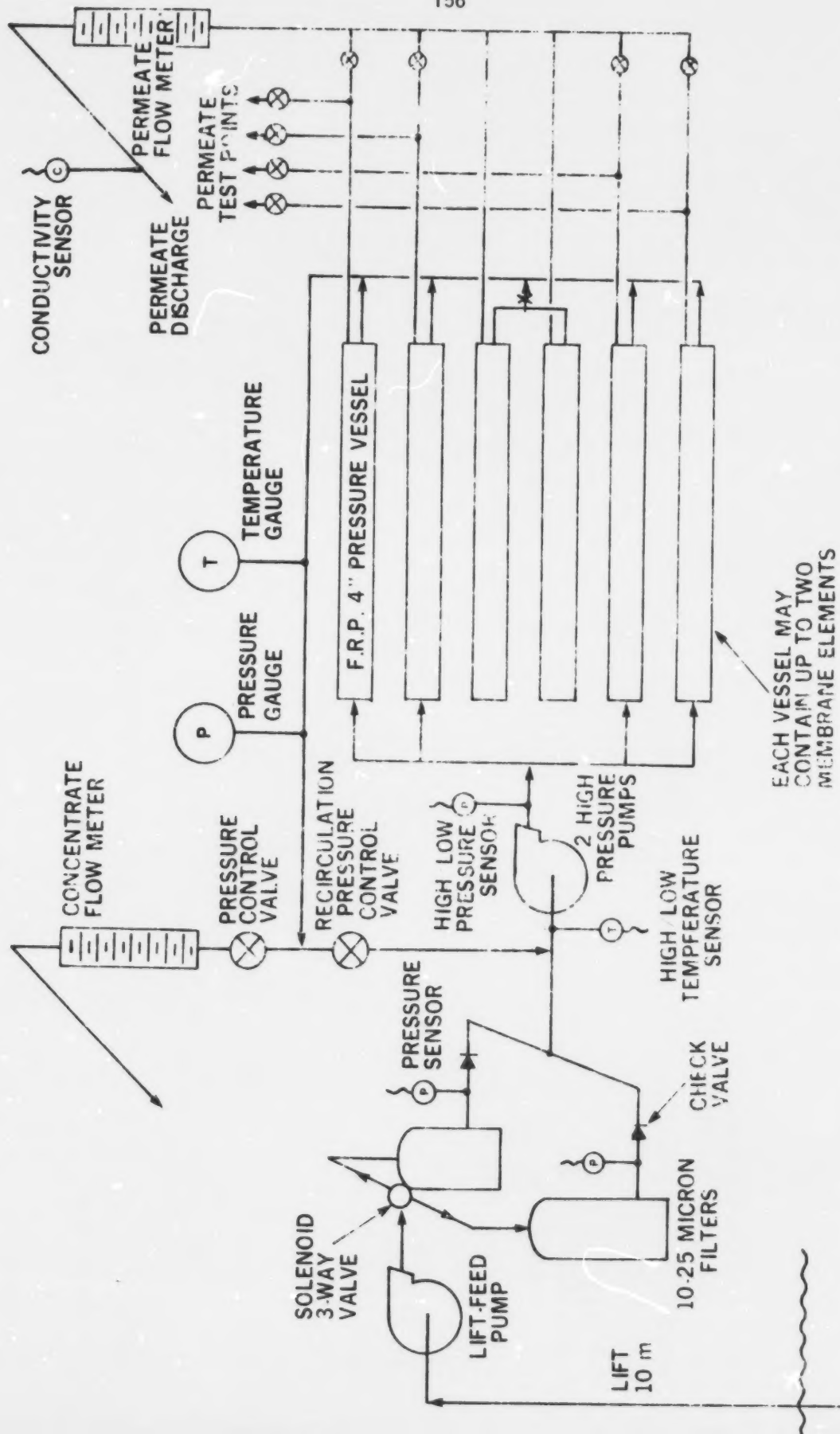


Figure 4 - RO Unit as configured for Testing

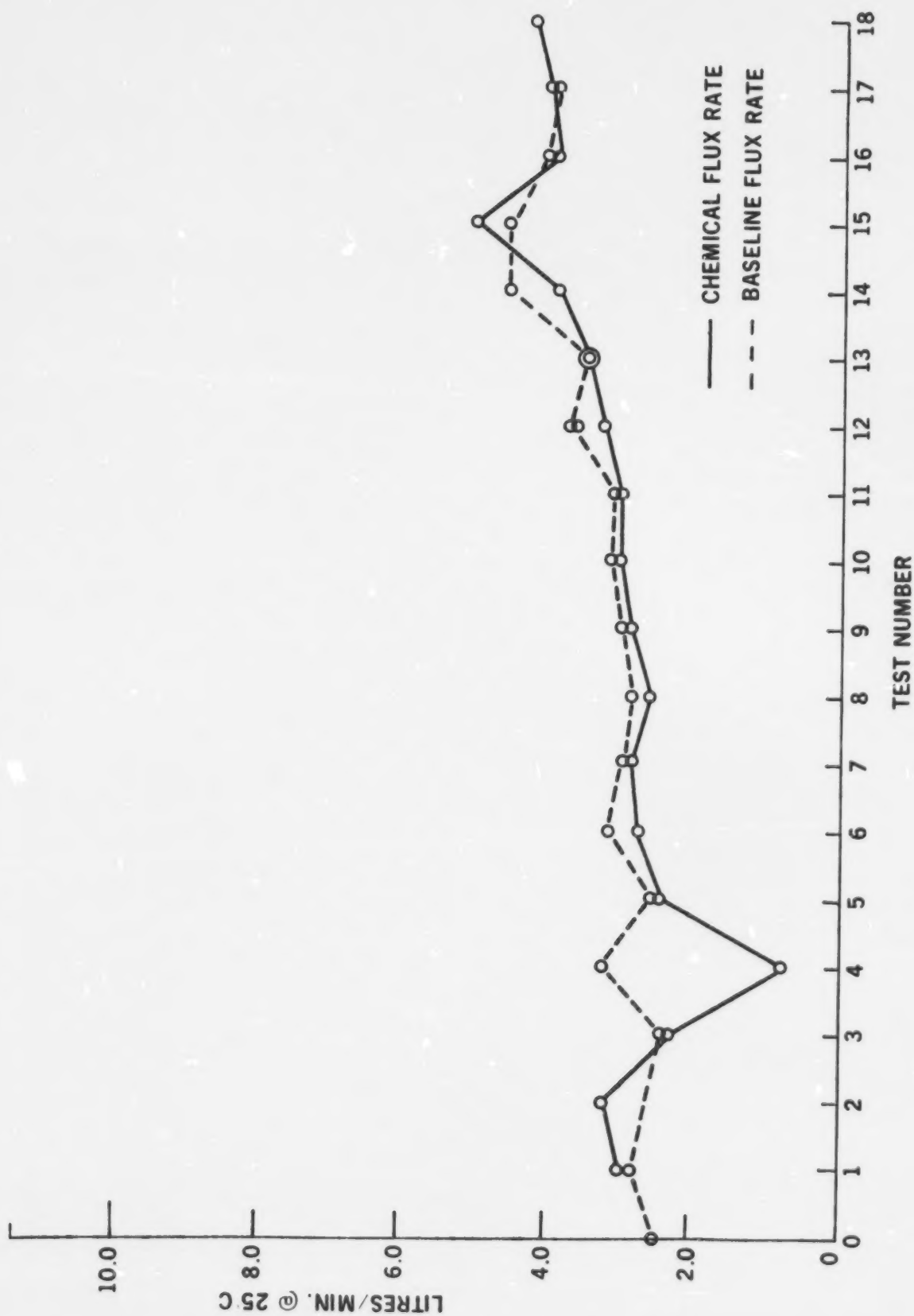


Figure 3. TORAY MEMBRANE FLUX RATES

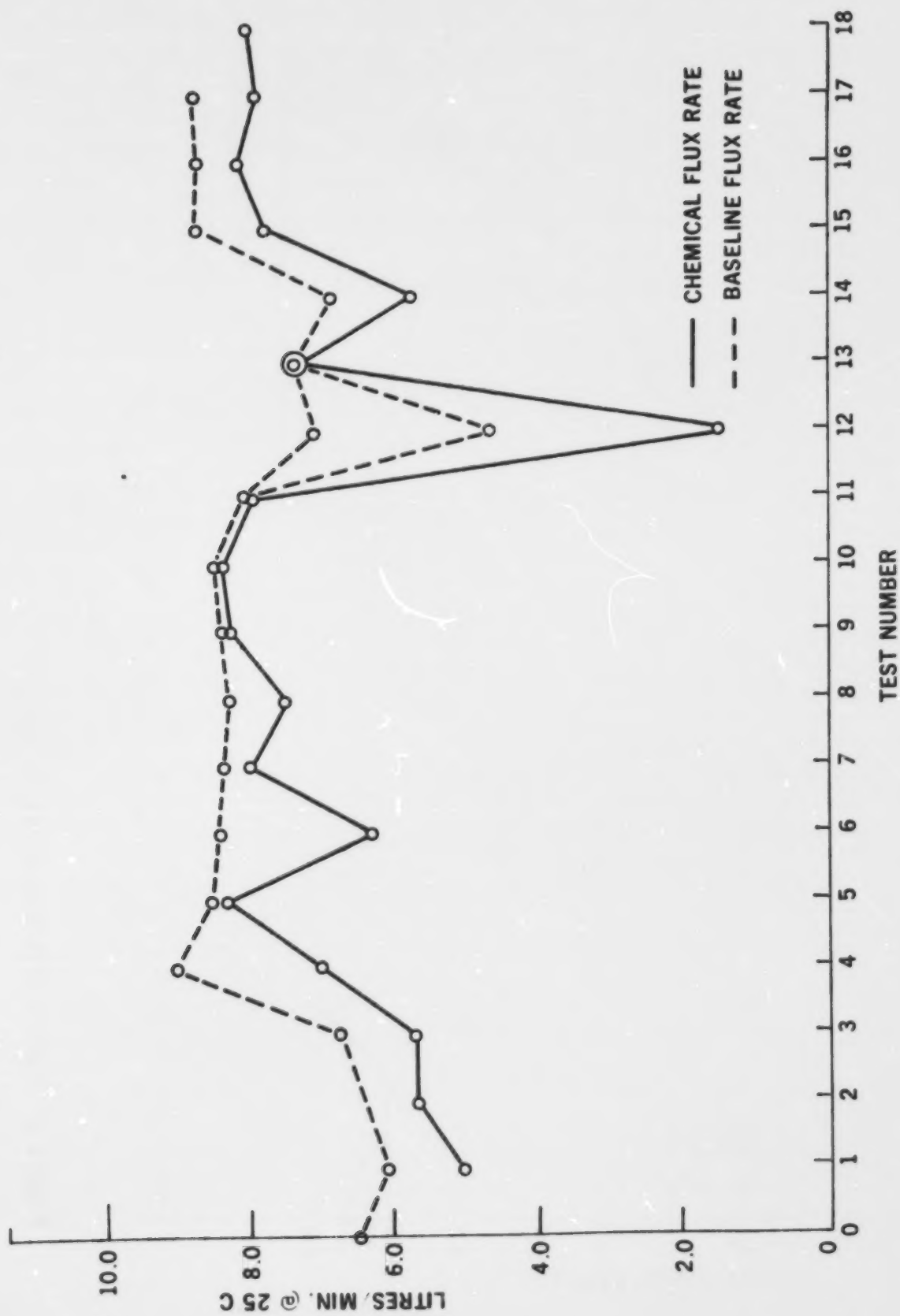


Figure 4. UOP MEMBRANE FLUX RATES

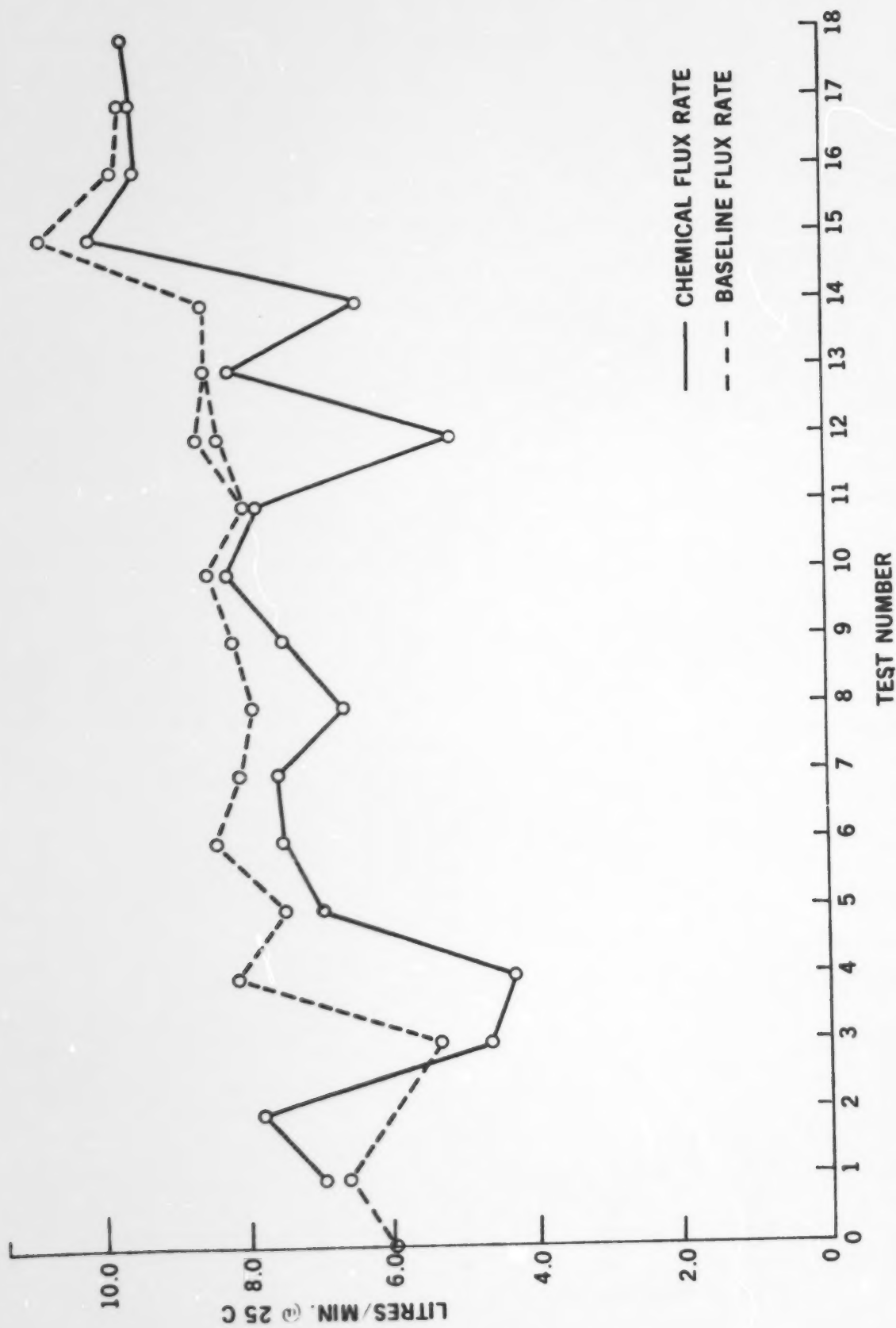


Figure 5. DESALINATION MEMBRANE FLUX RATES

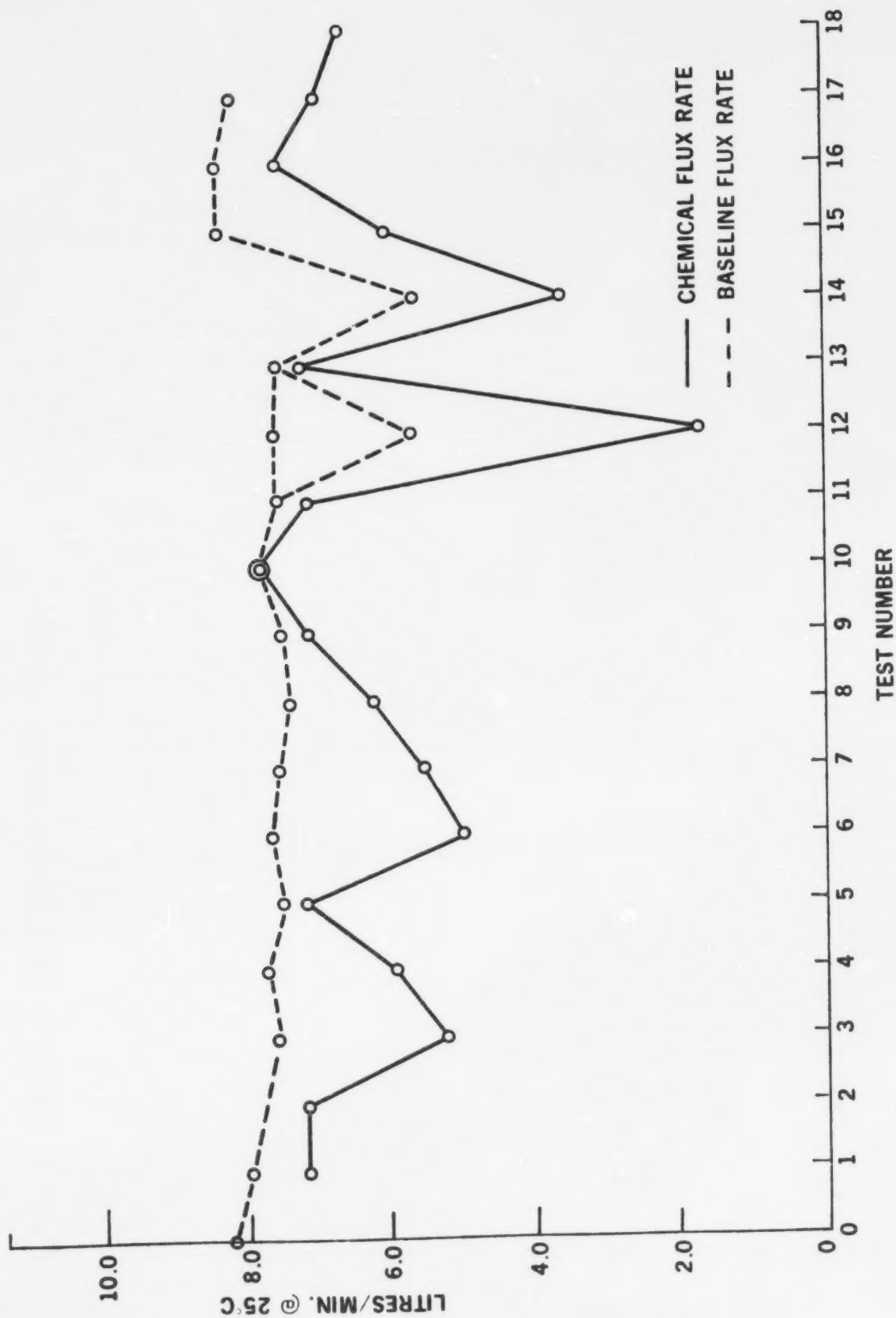


Figure 6. FILMTEC MEMBRANE FLUX RATES

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A SIMPLE MICRO-COMPUTER MODEL
OF SHORT AND LONG TERM CHEMICAL
SPILL BEHAVIOUR ON LAND

John D. Phyper

Donald Mackay

Department of Chemical Engineering and Chemistry
University of Toronto

Abstract

A relatively simple model has been compiled which can be used to estimate the behaviour of a chemical spilled on soil. The model treats the processes of infiltration into soil, interaction with ground water, sorption, evaporation, dissolution and degrading reactions. It can be run on a micro-computer of modest memory. By breaking the spill into four distinct time periods the equations are greatly simplified. A novel method is employed to combine the equations describing the various interacting process rates.

INTRODUCTION

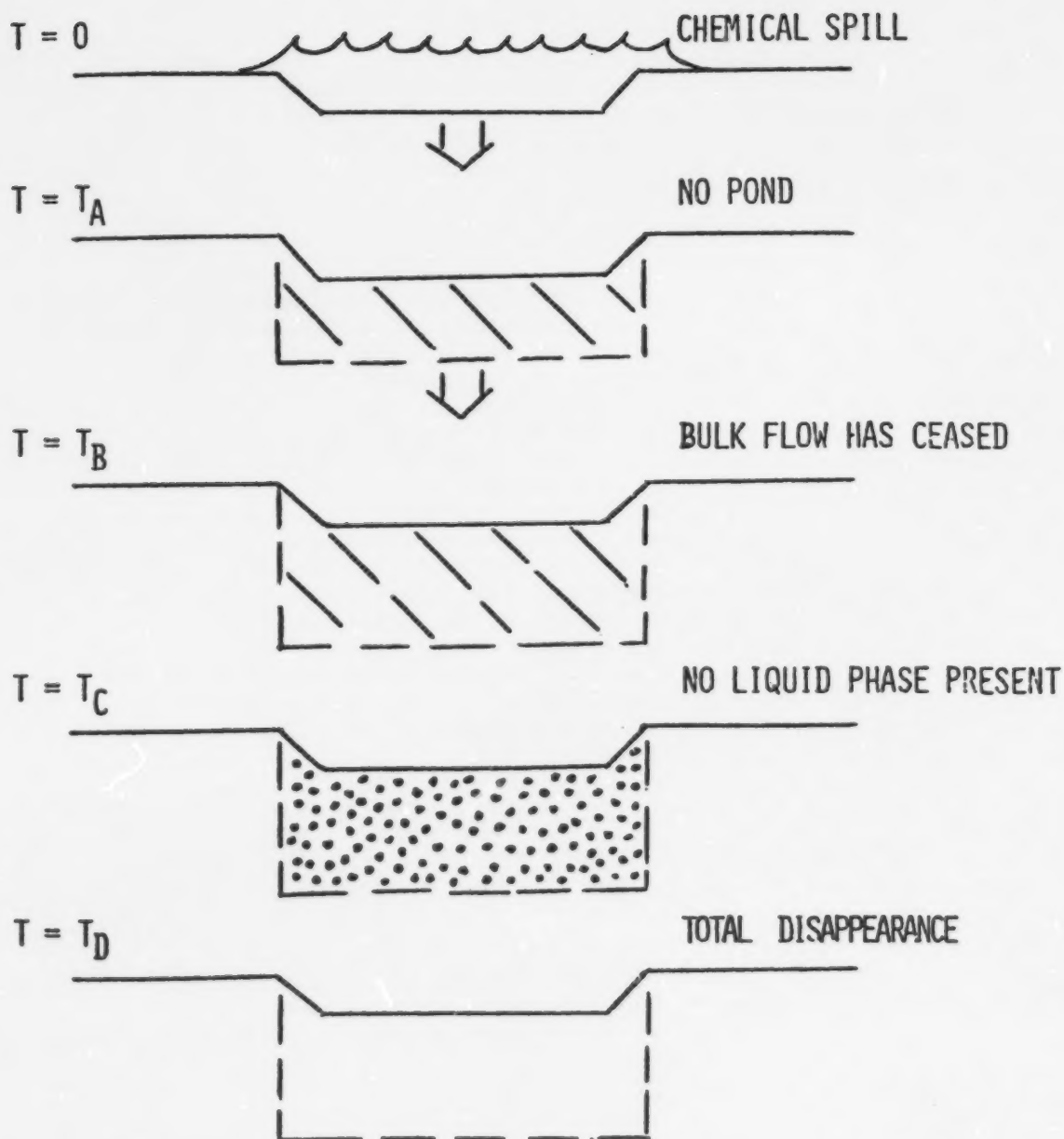
When a liquid chemical is spilled on soil it is valuable to be able to predict its behaviour as it evaporates, flows into and adsorbs onto the soil matrix, reacts, and is transported vertically by diffusion and convection in the air and water phases within the soil. Several time scales are of interest after a spill occurs. While the liquid exists as a pool or pond on the soil surface there may be a fire or toxicity hazard from vapors. After penetrating into the soil, the chemical may continue to migrate downwards causing groundwater contamination. Even after the bulk flow of the chemical has ceased the chemical may continue to evaporate and dissolve in water for a prolonged period and thus act as a continuing source of contamination.

MODEL FORMULATION

In this work we present a series of relatively simple mathematical models which describes the general behaviour characteristics of a liquid chemical spill, each model applying for a defined sequential time interval. Figure 1.0 illustrates the physical occurrence during a particular time interval. At time $t=0$, the spill occurs and infiltration and evaporation begin. In the first time period, t_a , the chemical infiltrates downward as a saturated front until the surface pond disappears. During the second period, t_b , the bulk flow continues to infiltrate until its movement is halted by an obstruction or by there being insufficient chemical volume to occupy all the available residual porosity. In the third period, t_c , the partitioning of the chemical into the soil, water and air phases is treated and removal is by reaction, evaporation and dissolution in water. This period ends when the pure chemical phase disappears. In the last time period, t_d , the removal of the partitioned chemical is treated, until it is ultimately totally removed.

By using the models in series, two significant benefits are gained. The short and long term effects are separated and there are considerable simplifications in the mass balance expressions that enable the complex system of equations to be reduced to a series of analytical equations. No longer do all the processes have to be included at all times since their influence may be assumed to be negligible for certain periods.

TIME PERIODS



Period A

During the first period the liquid is ponded on the soil surface with a decreasing depth as it evaporates and flows into the soil. This period ends when the pool depth becomes zero which may take minutes to hours. Three processes are considered, evaporation, infiltration into the soil, and reaction.

The evaporation rate of liquids has been discussed by Stiver and Mackay (1) who have shown that for a pure liquid of constant vapor pressure the evaporation rate N_{ea} , mol/h, is given by

$$N_{ea} = K_{og} A P_s / (R T) \quad (1)$$

where K_{og} (m/h) is the overall evaporation air phase mass transfer coefficient, A (m²) is spill area, P_s (Pa) is the chemical's vapor pressure, R is the gas constant (8.314 Pa m³/mol K) and T is absolute temperature (K). If the spill volume is initially V_{ao} (m³) its initial pond depth, H_{po} (m), is calculated as V_{ao}/A and its amount (mol) is V_{ao}/v where v is the liquid molar volume (m³/mol). This evaporation rate could be employed in an Gaussian air pollution model as the emission rate from a point source.

The time for complete evaporation, t_e (h) in the absence of other processes, is thus

$$t_e = (V_{ao}/v)/N_{ea} = (V_{ao}/K_{og} A)/(P_s v/R T) = (H_{po}/K_{og})/H \quad (2)$$

where H is the dimensionless Henry's law constant or ratio of concentrations in the air phase (P_s/RT) to concentration in the liquid phase ($1/v$).

For permeation into soil, t_p (h), in the absence of other processes, we use a modified version of the "Green-Ampt" model employed by Bouwer (2).

$$t_p = Q_f (n H_a - (H_{po} - H_e) \ln((H_{po} - H_e + n H_a)/(H_{po} - H_e))) / (n^2 K_{rs}) \quad (3)$$

where n = (1 - Q_f)
 H_{po} = initial liquid pond head above the upper soil surface (m)
 H_a = penetration depth at which there no longer exists a pond at the soil surface (m)
 Q_f = fillable porosity (m³/m³)
 H_e = effective suction head or negative pore pressure head (negative) (m)
 K_{rs} = resaturated hydraulic conductivity as found above the wetting front (m/h)

The fillable porosity of the liquid (typically 0.5) is taken as being equal to the soil air porosity Q_a . It is assumed that no liquid was present in the soil at time zero. The residual porosity (used later) is the volumetric fraction of the soil that the liquid occupies which does not continue to migrate downward as a result of the gravitational force but remains in place because of surface tension. It is typically 0.2 .

The effective suction head for water ranges from -10 cm for coarse soil material to -100 cm or less for fine grained material (3). The suction head is also a function of the initial moisture content of the soil and the nature of the infiltrating liquid.

The value of H_a , depth of penetration, used in period A is the liquid depth in the soil when the pond disappears. The assumption that the liquid has saturated the available porosity is used.

$$H_a = V_{ao}/(Q_a A) = H_p/Q_a \quad (4)$$

where Q_a is the volumetric air fraction (m^3/m^3) and is equal to the maximum void space that liquid may occupy. In reality the air is replaced by the liquid until residual air saturation is reached (4).

At this stage the depth H_a can be compared with the water table depth H_w or the depth of an impenetrable layer H_i . If H_a exceeds either value horizontal motion may occur. If the model predicts that infiltration has reached the water table then groundwater contamination has occurred. The concentration of contamination in the groundwater is discussed later in Period C. If the liquid density is less than that of water H_a is set equal to the water table depth. If the model predicts that an impenetrable layer has been reached H_a is set equal to the impenetrable layer depth.

There are several methods of combining these two processes and that of reaction. Rigorous combination requires that the interaction of parameters between evaporation, infiltration and reaction be included in the differential mass balance equation, but this leads to a very complex expression. A simpler method which is believed to be sufficiently accurate for the present purposes is to calculate all the three times and their corresponding rates (ie. evaporation, infiltration and reaction) in isolation and assume that they are a series of independent parallel occurrences. Each time is inversely proportional to the rate of the process and the rates are additive, ie.

$$N_{ta} = N_{ea} + N_{pa} + N_{ra} \quad (5)$$

where N_{ta} (mol/h) is the total rate. The time for total disappearance of the pool, t_a (h), can be estimated as

$$t_a = 1 / \{1/t_e + 1/t_p + K_{ra}\} = (V_{ao}/v) / N_{ta} \quad (6)$$

Here K_{ra} is the first order rate constant for degrading reactions. The amount of chemical removed in the processes of evaporation and reaction are then calculated by multiplying the initial amount by the ratio of the process time to the overall time. The amount remaining is also calculated.

The actual permeation distance into the soil, H_a is less than that calculated previously and is estimated by

$$H_a = (V_{ao} t_a / t_p) / (A Q_a) = H_p t_a / (t_p Q_a) \quad (7)$$

As with the initial calculation of H_a a comparison of (i) H_a to the impenetrable layers depth, (ii) H_a to the water table depth and (iii) density of the chemical to that of water is required. If the water table has been reached and the chemical's density is less than that of water or an impenetrable layer has been reached period B is skipped. In the case of reaching the water table, initially the liquid may penetrate temporarily below the water table as a result of a pressure build-up. As the infiltrating volume is usually limited, the pressure mount formed initially flattens eventually (4). The chemical is now located in the capillary fringe.

If the bulk flow has ceased as a result of the water table or an impenetrable layer, horizontal motion may occur increasing the spill area toward a new value A_n at which the soil is saturated, namely

$$A_n = M_{co} v / (H_w Q_r) \text{ or } H_a A / H_i \quad (8)$$

PERIOD B

Now that the liquid pond has disappeared in Period A, Period B begins. In this period the liquid which is now entirely subsurface, continues to flow downward for hours or days until bulk flow ceases. This can be the result of - the liquid either having insufficient volume to occupy all the available residual capacity of the soil, a barrier of lower permeability has been reached or a liquid with a density less than that of water has reached the saturated zone. In the second and third cases horizontal motion may occur.

A similar approach to period A is taken to calculate the time required for the three processes. For evaporation, it is

assumed that in addition to the soil surface boundary layer resistance characterized by Kog there is a diffusive resistance in the soil, Ks . The mass transfer resistance in the soil is calculated using the unsteady state or penetration expression for average mass transfer coefficient as described by Sherwood, Pigford and Wilke (5).

$$Ks = (4 De / (3.14 tpb))^{0.5} \quad (9)$$

where De , (m^2/h), is the effective diffusivity. In the above equation the time used is that required for the bulk flow to cease as calculated from equation 11. This assumption is based on the observation that for most chemicals tpb will be less than the time required for complete evaporation.

For permeation the maximum depth Hb is given by

$$Hb = Vbo / (Qr A) \quad (10)$$

where Qr is the residual porosity. The proposed penetration depth, Hb , is then compared to the water table depth or an impenetrable layer as was done with the Ha value in period A.

During this time period the driving force for flow is a combination of the suction head and the incipient pond depth. No longer is there a surface pond. The time required for infiltration is now

$$tpb = \frac{(Qf/Krs)(Hb-Ha) \{Ha + ((Ha Hb)/(Hb-Ha) - He) \ln((Ha-He)/(-He))\}}{Ha^2} \quad (11)$$

The reaction rate is included as a first order rate constant Krb which may differ from Kra if for example photolysis contributes to the surface reactions during period A but not during period B.

The time of period B is then estimated as before as

$$tb = 1 / (1/teb + 1/tpb + Krb) \quad (12)$$

The final permeation depth Hb is less than the previously calculated value and is estimated by

$$Hb = (Vbo tb / tpb) / (A Qr) = Vco / (A Qr) \quad (13)$$

As with the value of Ha at the end of period A calculations the value of Hb is compared to the water table depth or an impenetrable layer. If required, a new spill area is calculated. The amount remaining, at the end of period B and

the start of period C, is V_{co} , which is equal to $V_{bo} \text{ } t_b/t_{pb}$.

PERIOD C

For period C the bulk flow of the liquid has ceased. The time period required for the liquid phase to disappear is examined. The liquid phase undergoes sorption, evaporation, dissolution in water and reaction, resulting in a decrease in its amount until ultimately it reaches zero. The assumption of equilibrium between compartments is used in this period because of the prolonged contact time. The air, water and soil concentrations are taken as being saturated. It is convenient at this stage to transform the equations to fugacity form as described by Mackay and Paterson (6). This requires definition of the four fugacity capacities.

$$\text{air or vapor} \quad Z_a = 1/RT \quad (14)$$

$$\text{water solution} \quad Z_w = C_s/P_s \quad (15)$$

$$\text{sorbed in soil} \quad Z_s = K_p \rho \quad (16)$$

$$\text{pure liquid} \quad Z_l = 1/(P_s v) \quad (17)$$

where C_s is the aqueous solubility (mol/m^3), K_p is the sorption partition coefficient (L/kg) and ρ is the soil density (kg/L).

The volume of chemical in each of the four states totals to V_{co} . The amounts in each state are calculated from the fugacity capacities. During period C this volume falls to V_{do} which corresponds to the time at which the pure liquid vanishes. The amount removed is thus essentially the amount of pure liquid. The problem is then to calculate how long it takes for this amount to be removed. The rates of the removal processes are quantified in terms of D quantities, transport or transformation parameters (mol/Pa h), as introduced in earlier fugacity models. These are:-

$$\text{Evaporation} \quad D_{ev} = K_{gc} A Z_a \quad (18)$$

$$\text{where } 1/K_{gc} = 1/K_{og} + H_b/(2 D_{eb})$$

$$\text{Water Dissolution} \quad D_w = J A Z_w \quad (19)$$

$$\text{Reaction} \quad D_r = k_i V_i Z_i \quad (20)$$

In the above expression D_{eb} is the effective diffusivity of the chemical in soil. In equation 19 J is the vertical water

flow (m/h) a result of precipitation or irrigation. k_i is the rate constant in phase i of volume V_i and fugacity Z_i . The overall time period for the pure phase of the liquid to disappear can now be calculated from

$$t_c = (V_{co} - V_{do}) / (f \cdot v \cdot (D_e + D_w + D_r)) \quad (21)$$

where f is the equilibrium fugacity and is equal to the vapor pressure.

If groundwater contamination has been predicted in period B the primary concern is to find the maximum contaminant concentration in water that may be achieved. Depending upon the chemical's density the region of maximum concentration may be either in the upper or lower section of the saturated zone. In the latter however the concentration in the saturated zone would be more uniform since the chemical has passed through the region dissolving and leaving residual amounts behind.

In the saturated zone diffusion is the dominant process since dispersion is limited by the laminar flow conditions. The result is that the movement of the chemical is controlled by its diffusion rate. As a result of this the assumption of equilibrium conditions occurring in the contact area is put forth.

PERIOD D

It can be shown that the overall rate constant for removal during this period, K_d (1/h), is

$$K_d = (D_{ev} + D_{wd} + D_r) / \sum (V_i Z_i) \quad (22)$$

where V_i is the volume of each phase in which removal takes place. Since the processes are first order (which results in an exponential disappearance of the chemical), the overall time period is not as useful as the half life of the chemical for studying the environmental hazard of the situation. The half life is the time at which half of the chemical will still be present in the soil.

$$t_{0.5} = 0.693 / K_d \quad (23)$$

An overall time period can be found by adding t_a , t_b , t_c and t_d .

The equations derived here provide a physically reasonable description of the flow, reaction, evaporation, dissolution and sorption processes. They have been combined in a relatively

simple interactive computer program that requires a small memory allocation. It is emphasized that the primary contribution here is to structure the equations and compile the model in easily usable form. The parameter input values are in many cases suspect, primarily because there is a lack of data. The best approach is to "fit" the model to actual spill data. This is the thrust of current efforts.

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AAR'S Industrial Chemical Accident Response Information System

G. E. Meier, Association of American Railroads

Abstract

Many information sources present worthwhile data concerning hazards and responses for accidental chemical spills. Most sources, however, consider only the acute effects of a spilled substance and provide little information concerning the long term cleanup. Long term cleanup is typically considered unrelated to the emergency response. This concept is erroneous and costly. To combat this problem, the Association of American Railroads has undertaken a program to bridge the gap between first response and longer term environmental cleanup. The Computer information systems (ICARIS) was developed and integrated with a series of environmental/mathematical models to allow real time assessment of chemical release problems.

The design considerations inherent in this systems promote the evaluation of the long term consequences associated with emergency spill response activities.

This paper will describe the current capabilities of the computer information system.

ICARIS

AAR'S Industrial Chemical Accident Response Information System

Introduction

The first response actions utilized to control a chemical spill may have a profound impact on the long term cleanup of the spill. Information generally available to first responders is limited in scope and usually presents few data with which to evaluate long term cleanup problems. An even greater limitation of many information sources is the fact that they may be tied to one or two spill situations with no provisions accounting for the uniqueness of an individual spill.

In 1979 the Association of American Railroads began an intensive effort to collect information describing those commodities commonly carried nationally by rail.

During the data collection phase, potential users were identified as railroad response personnel, chemists, biologists, and others with an environmental/chemical background.

The data collected by AAR for presentation consists of 180 descriptive entries per commodity, grouped into four major categories.

1. General Information -- This includes 48 elements to identify the chemical including synonyms, tradenames, the different codes (IMCO, STCC, UN), useful shipping information, and some physical constants.
2. Chemical Information -- Included 35 elements that describe the chemical properties of each chemical.
3. Health and Hazard Information -- This consists of 40 data elements describing the hazards of an uncontrolled release of the chemical including response guidelines, health hazards, and protective clothing needed.

4. Environmental Effects Information -- This section has 52 data elements including toxicity, pollution effect, and interreaction data.

Each data point listed in Table 1 was collected from current and reliable sources. Each entry is referenced back to the original data to allow the user to identify which of the over 40 sources was used for that item of information.

The commodities characterized (listed in Table 2) were restricted to those moved in bulk quantity. Selection was based on the number of car loadings in decreasing order.

Presently, 134 commodities have been completed representing over 98 percent of the railroad chemical traffic.

Computer Communication

The computer media was selected to provide the swiftest method of communicating large volumes of data as well as state of the art predictive information to trained responders on scene. This system known as ICARIS, (Industrial Chemical Accident Response Information System), is designed to mesh up-to-date chemical data with state of the art predictive modeling to provide the user with a dynamic method for assessing the adequacy of their response activities. ICARIS is housed on AAR's IBM 370 system and can be accessed by remote terminal over the telephone network.

The principal advantage of this system is that it allows a site specific analysis of a spill situation. The complex environmental interactions are discussed not in terms of broad generalities, rather the specific peculiarities of the location of the spill. This method allows a more complete and specific evaluation of the individual situation.

The major limitation of the system is tied directly to the current understanding of chemical/environmental interactions. The number of environmental variables that effect chemical behavior is quite large, and this

interaction is very complex. Hence, the use of spill models, at least presently, must be considered in light of the assumptions intrinsic to each model. This requires expertise and training not generally available to the first response community.

Presently, ICARIS performs three basic functions. These include data retrieval, air dispersion modeling, and chemical property estimation.

The design of the computer program is straight forward and requires a minimum of computer training for operation. Generally, the system is menu driven presenting the user with a question and a fixed set of choices. The main menu, Figure 1, allows the user to select from among the five major packages currently on line. Option 1 is a search that allows the user to print data organized into pre-arranged categories of information for each commodity requested. Option 2 allows the user to print individual items of information as needed. Option 3 allows the user to select any number of chemicals which produces a chemical by chemical printout of all the reaction information contained in the data base. Option 4 involves the evaporation air dispersion model allowing the calculation and subsequent plotting of the vapor dispersion for a given area. The model currently in use is the Shell Development Corporation's Spills Model written by M. T. Fleischer. Option 5 allows the user to select from among 19 techniques for calculating various chemical properties.

The estimation techniques in Option 5 were included because many of the properties contained, such as rate of hydrolysis, carbon absorption ratios, thermal diffusivity, and volatility from soil, are either site dependent or not reported in the literature. These data are often necessary for the prediction of a chemical's behavior in air, water, or soil.

The last option, Number 6 allows the user to terminate processing within ICARIS.

Future Developments

Future enhancements to ICARIS will come in three basic areas:

1. Increase in commodity coverage,
2. Increase in data describing each commodity, and
3. Increase in the number and reliability of environmental models.

Items 2. and 3. are dependent on basic research into the behavior of chemicals in the environment. The use of ICARIS as a preplanning and training tool is also being explored.

Summary

Safety in transportation is a primary concern of the U. S. rail industry. The research conducted in tank car design, head shields, shelf couplers, and thermal protection has contributed enormously to the reduction in the type of accidents observed 15 years ago. Recognizing, however, that some accident factors are uncontrollable, handling an accident properly is of paramount importance. This work, as well as other programs such as the development of a chemical/medical reference and the identification of chemical combustion products, is targeted at increasing the understanding of spill behavior. Through this understanding, better and faster cleanup technologies and management will undoubtedly result.

Through ICARIS, state of the art assessment of a spill can occur. Improvements to ICARIS will come as the science of chemicals in the environment becomes more advanced.

Data Fields

Table 1

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- | | |
|---------------------------------|-------------------------------|
| 1. Acetaldehyde | 24. Butyraldehyde |
| 2. Acetic Acid, Glacial | 25. Calcium Carbide |
| 3. Acetic Anhydride | 26. Carbohc Acid or Phenol |
| 4. Acetone | 27. Carbon Bisulfide |
| 5. Acetone Cyanohydrin | 28. Carbon Dioxide, Liquefied |
| 6. Acrolein | 29. Carbon Tetrachloride |
| 7. Acrylic Acid | 30. Chlorine |
| 8. Acrylonitrile | 31. Chlorobenzene |
| 9. Adipic Acid | 32. Chloroform |
| 10. Allyl Chloride | 33. Chloroprene |
| 11. Ammonium Hydroxide | 34. Chlorosulfonic Acid |
| 12. Ammonium Nitrate Fertilizer | 35. Chromic Acid |
| 13. Anhydrous Ammonia | 36. Creosote |
| 14. Aniline Oil, Liquid | 37. Cresol |
| 15. Arsenic Trioxide | 38. Cyclohexane |
| 16. Asphalt | 39. Di-N-Propylamine |
| 17. Benzene | 40. Dichlorodifluoromethane |
| 18. Bromine | 41. Diisobutylene |
| 19. Butadiene, Inhibited | 42. Dimethylamine, Anhydrous |
| 20. Butene | 43. Epichlorohydrin |
| 21. Butyl Acetate | 44. Ethyl Acetate |
| 22. Butyl Acrylate | 45. Ethyl Acrylate, Inhibited |
| 23. Butyl Alcohol | 46. Ethyl Alcohol |

Table 1 continued

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- | | |
|---|---------------------------------------|
| 47. Ethyl Chloride | 68. Isobutyl Acetate |
| 48. Ethylene | 69. Isobutyraldehyde |
| 49. Ethylene Glycol Monoethyl-
ether | 70. Isopentane |
| 50. Ethylene Glycol Monoethyl-
ether Acetate | 71. Isoprene |
| 51. Ethylene Oxide | 72. Isopropanol |
| 52. Ferric Chloride Solution | 73. Liquefied Petroleum Gas |
| 53. Formaldehyde | 74. Maleic Anhydride |
| 54. Fuel Oil No. 1 | 75. Meta Nitrochlorobenzene |
| 55. Fuel Oil No. 2 | 76. Methanol |
| 56. Fuel Oil No. 4 | 77. Methyl Bromide |
| 57. Fuel Oil No. 5 | 78. Methyl Chloride |
| 58. Furfuryl Alcohol | 79. Methyl Ethyl Ketone |
| 59. Gasoline | 80. Methyl Isobutyl Ketone |
| 60. Hexamethylene Diamine | 81. Methyl Mercaptan |
| 61. Hexane | 82. Methyl Methacrylate |
| 62. Hydrochloric Acid | 83. Monochlorodifluoromethane |
| 63. Hydrocyanic Acid, Liquefied | 84. Monoethanolamine |
| 64. Hydrofluoric Acid, Anhydrous | 85. Monomethylamine, Anhydrous |
| 65. Hydrofluosilicic Acid | 86. Motor Fuel Antiknock
Compounds |
| 66. Hydrogen Chloride | 87. Nitrating Acid |
| 67. Hydrogen Peroxide, Solution | 88. Nitric Acid, Fuming |
| | 89. Nitrobenzene |

Table 1 continued

90. Octanol	112. Sodium Hydrosulfide
91. Oleum	113. Sodium Hydrosulfite
92. Ortho Nitroaniline	114. Sodium Hydroxide
93. Ortho Nitrochlorobenzene	115. Sodium Metal
94. Para Nitrochlorobenzene	116. Sodium Nitrate
95. Pentane	117. Spent Caustic Soda Solution
96. Petroleum Naptha	118. Spent Sulfuric Acid
97. Phosphatic Fertilizer	119. Styrene Monomer, Inhibited
98. Phosphoric Acid	120. Sulfur Chloride
99. Phosphorus Pentasulfide	121. Sulfur Dioxide
100. Phosphorus	122. Sulfuric Acid
101. Phosphorus Trichloride	123. Tetrahydrofuran
102. Potassium Hydroxide Solution	124. Thorium Ore
103. Potassium Nitrate	125. Titanium Tetrachloride
104. Propionaldehyde	126. Toluene
105. Propionic Acid	127. Toluene Diisocyanate
106. Propyl Acetate	128. Trichloroethylene
107. Propylene Oxide	129. Trimethylamine
108. Rosin Solution	130. Uranium Hexafluoride
109. Silicon Chloride	131. Vinyl Acetate
110. Sodium Chlorate	132. Vinyl Chloride
111. Sodium Cyanide, Solid	133. Vinylidene Chloride, Inhibited
	134. Xylene

Commodities Listing

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Table 2

1	Commodity Name	49	Specific Gravity (Liquid)
2	Other Shipping Names	50	Specific Gravity (Vapor)
3	Synonyms and Tradenames	51	Density
4	Chemical Formula	52	Density at Shipping Temperature
5	Molecular Weight	53	Vapor Pressure
6	Constituent Components (% Each)	54	Vapor Pressure at Shipping Temperature
7	49 STCC	55	Solubility in Water
8	CAS Registry Number	56	Solubility in Other Chemicals
9	OHM-TADS Accession Number	57	Solution Color
10	Standard Industrial Code	58	Melting Point
11	IMCO Designation	59	Freezing Point
12	UN Designation	60	Melting/Freezing Behavior
13	CHRIS Identifier	61	Boiling Point
14	Manufacturers	62	Boiling Behavior
15	Common Uses	63	Heat Capacity (Constant Pressure)
16	Percentage Shipped by Rail	64	Heat Capacity (Constant Volume)
17	Usual Containers	65	Heat of Combustion
18	DOT Placard and Form Number	66	Heat of Decomposition
19	Physical State as Shipped	67	Heat of Solution
20	Physical State as Released	68	Latent Heat of Vaporization
21	Shipping Temperature	69	Latent Heat of Fusion
22	Color	70	Latent Heat of Sublimation
23	Odor Characteristics	71	Thermal Conductivity
24	Threshold Odor Concentration	72	Thermal Conductivity at Shipping Temperature
25	Absolute Odor Threshold	73	Surface Tension
26	Median Recognition Threshold	74	Interfacial Tension With Water
27	Upper Recognition Threshold	75	Viscosity
28	Population Perception Threshold	76	Viscosity at Temperature
29	Population Identification Threshold	77	Saturation Concentration
30	Individual Perception Threshold	78	Saturation Concentration at Shipping Temperature
31	Threshold Odor Number	79	Diffusivity
32	Odor Index	80	Diffusivity at Shipping Temperature
33	Taste Characteristics	81	Polymerization Potential
34	Lower Taste Threshold	82	Heat of Polymerization
35	Median Taste Threshold	83	Reactivity With Water
36	Upper Taste Threshold	84	Reactivity With Other Chemicals
37	Flash Point	85	Toxic Reaction Products
38	Lower Flammable Limit	86	Vapor Weight-Volume Conversion Factor
39	Upper Flammable Limit	87	Emergency Resources
40	Lower Explosive Limit	88	Emergency Telephone Numbers
41	Upper Explosive Limit	89	Notification Requirements
42	Explosiveness	90	Public Health Hazards
43	Autoignition Temperature	91	Evacuation Guidelines
44	Burning Rate	92	Incompatible Materials
45	Toxic Combustion Products		
46	Behavior in Fire		
47	Electrical Ignition Hazard		
48	Stability		

Table 2 continued

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93	Conditions to Avoid	131	Avian Species
94	Unusual Hazards	132	Plant Species
95	Corrosiveness	133	Human Toxicity
96	NAS Hazard Classification	134	Bioaccumulation Potential
97	NFPA Hazard Classification	135	Food Chain Concentration Potential
98	Field Detection, Identification, and Quantification Techniques	136	Threshold Limit Value
99	Field Detection Limits	137	Other Standards
100	Laboratory Detection, Identification, and Quantification Techniques	138	Recommended Drinking Water Limit
101	Laboratory Detection Limits	139	Inhalation Toxicity Index
102	Containment Techniques for Airborne Materials	140	Maximum Pool Radius/Spill Size
103	Containment Techniques for Ground Contamination	141	Diameter at Base of Solid Pile/ Spill Size
104	Containment Techniques for Surface Water Contamination	142	Fugitive Dust or Particulate Emissions
105	Containment Techniques for Ground Water Contamination	143	Maximum Downwind Extent of Vapor Cloud/Bounding Effect/Spill
106	Neutralization Materials	144	Maximum Crosswind Extent of Vapor Cloud/Bounding Effect/Spill
107	Neutralization Techniques	145	Total Hydrocarbon Emissions
108	Extinguishing Materials	146	General Air Pollution Information
109	Extinguishing Techniques	147	Downstream Concentration Factor
110	Symptoms of Inhalation	148	Sinking Velocity
111	First Aid for Inhalation	149	PH of Aqueous Solution
112	Symptoms of Percutaneous Absorption	150	Biological Oxygen Demand
113	First Aid for Percutaneous Absorption	151	BOD impact on Biodegradation
114	Symptoms of Ingestion	152	Biodegradation Rate
115	First Aid for Ingestion	153	Chemical Oxygen Demand
116	Aspiration Potential	154	Theoretical Oxygen Demand
117	Nonspecific Symptoms	155	Total Organic Carbon
118	Nonspecific First Aid	156	Industrial Water Fouling Potential
119	Time to Onset of Symptoms	157	Effects on Water Treatment Process
120	Routes of Entry	158	General Water Pollution Information
121	First Aid Equipment Required	159	General Soil Chemistry
122	Respiratory Protection Required	160	Soil Penetration Depth/Soil Type/ Soil Dosage
123	Protective Clothing Required	161	Minimum Soil Sterilization Concentration
124	Location of Primary Hazard	162	Estimated Half-Life in Soil/ Soil Type/Soil Dosage
125	Safe Handling Procedures	163	Estimated Diffusion in Soil/ Soil Type/Soil Dosage
126	Precautionary Actions	164	Absorption Materials/Absorption Techniques/Absorption
127	Short-Term Exposure Limits (Maximum Time/Maximum Concentration)	165	Adsorption Materials/Adsorption Techniques/Adsorption
128	Freshwater Species	166	Activated Carbon Dosage/ % Reduction by Activated Carbon Adsorption
129	Saltwater Species		
130	Animal Species		

Table 2 continued

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- 167 Gelation Materials/
Gelation Techniques/
Gelation Effectiveness
- 168 General Cleanup Information
- 169 Availability of Countermeasure
Materials
- 170 In-Situ Amelioration Techniques/
In-Situ Amelioration
Effectiveness
- 171 Onsite Disposal Limitations
- 172 Chronic Hazards
- 173 Synergistic Materials (Toxicity)
- 174 Antagonistic Materials (Toxicity)
- 175 Environmental Fate
- 176 Toxic Daughter Products
- 177 Sampling Locations
- 178 Disposal Techniques/Disposal
Effectiveness
- 179 Required Agency Coordination
- 180 General Disposal Information

Figure 1**ICARIS Main Menu**

```
*****
*                                     *
*                                     *
*          ICARIS                     *
* INDUSTRIAL CHEMICAL ACCIDENT RESPONSE INFORMATION *
*          SYSTEM                     *
*                                     *
*          THE ASSOCIATION OF AMERICAN RAILROADS   *
*          1983                               *
*                                     *
*****
```

ARE YOU OPERATING A HARDCOPY TERMINAL?
ENTER (YES/NO):NO

DO YOU NEED HELP?
ENTER (YES/NO):NO

WHAT TYPE OF SEARCH DO YOU WANT?

- 1= CATEGORICAL
- 2= ITEM BY ITEM OR RANGE
- 3= CHEMICAL SYNERGIES
- 4= AIR DISPERSION MODEL
- 5= CHEMICAL PROPERTIES ESTIMATION TECHNIQUES
- 6= QUIT

?

THE ROLE OF COMPUTERS IN CHEMICAL SPILL RESPONSE

D. Mackay

Department of Chemical Engineering & Applied Chemistry

University of Toronto

Introduction.

The purpose of this paper is to speculate on the role which computers may have in chemical spill response. The word "speculate" is emphasized. It is possible that some of the capabilities described here may not be attainable, but at least this material may serve as a starting point for debate. Two trends are evident which influence the role of computers in spill response.

First, we are clearly entering an era of much greater computer literacy. Not only are young people completely "at home" at the computer keyboard but they expect computers to be used wherever possible as tools to eliminate the drudgery of long calculations, sorting or searching for data and to provide the convenience of storing a mass of data in a small volume.

Second, there is a heightened public awareness of the inconvenience or even danger from toxic chemical spills. They thus expect fast, competent response using all available modern technologies - including the computer.

Rather than discuss the issue at some length we take the more direct approach of describing a future hypothetical situation in which a computer is used to assist response to a chemical spill. In some cases the computing capability already exists - in other cases it does not. But it is believed that the capability could exist in 10 years.

The Spill Scenario.

A tank truck skids off an icy highway at 2:00 a.m., on the night of February 13th., overturns in a clump of bushes near a bank, the tank is punctured and the contents start to leak generating a liquid pool in the ditch and a cloud of vapour. There is about an inch of snow on the ground. The police are first on the scene, alerted by a private CB radio, rapidly followed by the local fire department and an ambulance. The driver manages to crawl free but collapses and is taken unconscious to a local hospital. The immediate area is evacuated. The local fire chief arrives with her portable computer, printer, software and radio. She starts the process of computer spill response by inserting the first hard disk which brings up a program to help identify the spilled material. She also sets up a radio link with the National Spill Response Centre such that she can discuss the events with them and exchange data.

Identification.

The identification program asks a series of questions as

shown in Figure 1. There is some doubt about the chemical nature of the cargo because the placard is obscured. In this case the identification is complicated by the lack of visible confirming letters or numbers but eventually it is fairly certain that the cargo has been correctly identified as vinyl chloride monomer. An access number is noted and the computer gives instructions for a second disk to be inserted. This process is watched by the Response Centre who are now trying to contact likely owners of the vehicle and cargo.

Chemical Properties.

The properties program prompts for the access number then offers to display or print any desired information about the chemical's properties - physical chemical or toxicological. It has also stored certain critical data about the chemical for later use.

The printout gives a concise statement of the nature of the chemical, its likely behaviour and what precautions should be taken. In this case the primary concern is exposure by inhalation since the substance is toxic and carcinogenic (Figure 2).

Essentially, this disk contains the entire set of TIPS manuals and can print out the material as desired. Some additional information on vinyl chloride behaviour in snow is transmitted from the Centre to the site and is printed out.

Several problems face the fire chief. How long is this material going to leak, form a pool and evaporate? Should she leave the tank car alone or try to plug the leak? Should the local inhabitants be requested to evacuate and if so over what distance? To answer these questions she enlists the aid of the ENVIRONMENTAL BEHAVIOUR PROGRAMS.

The appropriate disk is inserted.

Environmental Fate and Behaviour.

The first task is to use the SPILL program to determine the type of spill and its volume, area of spread and depth. The most appropriate spill configuration is selected, in this case leakage of liquid from a road tanker with a single below-liquid-level hole. By estimating the hole size and the leakage rate visually, and entering these values in the program the leakage characteristics are estimated. The results seem to be reasonable.

The program asks for information about the local terrain, snow conditions, the weather etc. as a prelude to calculating the spill behaviour.

Since exposure by inhalation is important, the evaporation rate should be calculated using the EVAPORATION AIR DISPERSION program. A "source strength" is thus calculated for later use in an air dispersion calculation.

A simple air dispersion calculation is performed which gives estimated concentrations at various distances downwind. Also given is the proximity of these concentrations to short term effect levels and other concentrations of relevance. A fire hazard could also be estimated if desired.

Spill identification program

Our first task is to identify the spilled material. Please indicate by letter which information you have

Name or partial name	N
UN number	U
STCC number	S
OHM-TADS number	O

Enter appropriate letter:- N

Please enter the name:- VCN

VCN

Sorry I have no such chemical, try again

ACN

Sorry I have no such chemical, try again

MCN

Sorry. Do you want me to search for similarly named chemicals? Y/N

Y

The closest chemicals are:-

VCM (vinyl chloride monomer) No. 1086

VC (vinyl chloride) No. 1086

vinyl chloroacetate No. 2589

vinylidene chloride No. 1303

Acetonitrile No 1648

If any of these seem likely please enter their number.

1086

Fig 1

Tentative identification

Vinyl chloride monomer, sometimes designated as "inhibited" also known as VCM, VC, Chlorure de Vinyle, ethylene monochloride.

UN Number 1086

OHM TADS Number 7216947

STCC Number 4905792

This chemical is a gas which is normally shipped in the liquid compressed state in cylinders, (about 140 cm long by 26 cm diameter) or in one ton containers (about 200 cm long by 74 cm diam), or in 81 tonne railway tank cars (about 12 m long by 3 m diameter), or in road tanks, 15 to 20 tons (about 5 m by 2 m diameter). Tanks are usually insulated.

Principal manufacturers are Dow Chemical Canada (Sarnia) and Dow Chemical Canada (Fort Saskatchewan). Most frequent transport is to Ontario, Quebec and Alberta. Other suppliers are

Henley Chemicals, Pickering, Ontario

Kingsley & Keith (Canada), Montreal, P.Q.

St. Lawrence Chemical Co., Montreal, P.Q.

Fig 2

Vinyl chloride continued

It is a highly flammable, very toxic chemical with a faintly sweet odor. The liquid boils at -13 degrees C to form a heavy vapor. Its HAZCHEM action code is 2WE. Its NFPA classification is

Flammability 4
Health 2
Reactivity 1

Is this sufficient information to identify the chemical, please respond.

- Y - Yes it is confirmed to be this chemical
- N - Confirmed that it is not this chemical
- U - Unsure - please provide more information
- R - Return and try another chemical
- ? Y

The chemical is confirmed as vinyl chloride monomer.

Please record its UN No. for future reference 1086

Please remove disk and insert disk No. 4 to enter chemical properties.

FIG 2 CONTD

Chemical Properties Program

Enter Chemical No.

? 1086

Vinyl Chloride

Vinyl chloride is a volatile liquid which boils at -13 degrees C to form a heavy vapour (2.1 times the density of air) it is sweet smelling. Some properties are

Molecular weight 62.5
Liquid density 990 kg/m³
Flammability limits are 3.6 to 26.4%
Flash point -78 degrees C
Sparingly soluble in water
Viscosity is 0.3 mPas (water 1 mPas)

It is highly flammable. It is an irritant to eyes, nose and throat and causes dizziness, anaesthesia, breathing difficulties, headache and paralysis.

It is a proved carcinogen.

TLV is 5 ppm

Evacuate immediate area, call fire department, notify manufacturer, avoid contact with liquid or vapour.

For fire control use foam dry chemical, CO₂ or water.

Containers may explode in fire.

These and other data have been recorded. Press enter.

FIG 2 CONTD

The best strategy in this case seems to be to leave well alone, allow the tank to drain and the contents to evaporate. It seems wise to evacuate all residents within 1 km of the site and any sensitive individuals such as young children, pregnant women, asthmatics and the elderly or infirm within 2 km. The proper protective equipment for use by those in the spill area is specified.

But the Chief is also concerned that the liquid may penetrate deeply into the soil and contaminate local wells. She calls up the SOIL PENETRATION BEHAVIOUR program similar in principle to that described in these Proceedings by Phyper and is reasonably reassured.

By morning it has warmed up and started to rain quite hard and there is a possibility that the vinyl chloride monomer is going to be swept along the ditch and into a nearby creek. How serious is this threat? She calls up the AQUATIC SPILL program, in this case for a river. Fears that the chemical would sink to the river bottom are unfounded. It will probably float on the water surface but should evaporate within 300 m. It will not pose a long term threat to fish in the area. It does not bioconcentrate significantly. Precautions should be taken however to ensure that no one draws drinking water from the river in the next few days.

A GENERAL ENVIRONMENTAL FATE program is called up which paints a picture of where the chemical is likely to go, how long it will persist, which compartments are of greatest concern and especially where it should not be directed. This alleviates the concern of the local fishing lodge operator who had heard that some chlorinated hydrocarbons had been spilled into the river. He is relieved to hear that the material is not polychlorinated biphenyls but is some other chlorinated stuff.

By 11:00 a.m. the leak has stopped because the liquid level has fallen to that of the puncture. But some chemical remains in the tank. The Chief calls up the COUNTERMEASURES program to help suggest how to treat the remaining material. By this time a representative of the chemical company has arrived and between them, and with the help of the central spill response office they decide to apply a patch then attempt to right the truck. This is accomplished successfully, and safely and the truck is towed away to a more remote location where its contents can be transferred to a second truck. All is now well.

CONCLUSIONS.

All the services performed in this scenario are feasible and in many cases the programs already exist, but not necessarily in micro-computer format. There are certain obvious requirements and benefits.

(1) A small, light, battery-operated portable computer with hard disks can store an immense amount of factual information which is normally stored in text form on paper. Book manuals may become obsolete except as a permanent archival record of disk contents.

(2) It is technically feasible to supply on-scene personnel with text both from their own disks and from data stored in a

central mainframe computer by a telephone line or radio link. The on-scene people can then request as much detailed information as they want.

(3) It is important that the on-scene personnel be fully conversant with the programs, feel confident about using them and are not confused about units. This requires practice at "spill games" sessions.

(4) There is a strong incentive to back up these programs by having them run in parallel at a spill response centre, such that an "expert" can see what is being done. This requires a radio or telephone data link as well as a voice link. He may intervene if necessary if he believes that a mistake has been made. He may also serve as a link to weather forecasting services and to alert the cargo's owner and other interested parties. He should be in constant electronic contact with those at the spill site and should log all events as they occur. He may choose to run these or other programs himself to confirm the validity of the local output.

(5) The programs must be relatively simple, very robust and require only essential data. It may transpire that several versions of increasing complexity will be needed. In some cases, such as a PCB spill, a fairly complex soil or aquatic program may be needed, but only a simple air dispersion program is needed.

(6) Ultimately there is no substitute for informed human judgement and ingenuity. The computer should not be regarded as a replacement for such expertise, only as a supplementary tool to store large quantities of data for easy access, to perform certain relatively simple calculations, and to relieve those concerned of the need to guess the outcome of spill events. How many fire chiefs (let alone chemists) know the likely behaviour and health hazards of vinyl chloride, or hydrogen chloride, or calcium chloride or benzene hexachloride or ethylene dichloride?

Clearly the hi-tech world of computers has a role in spill response, but exactly what it will be, and when it will be, remains to be seen.

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REVERSE OSMOSIS AT THE
GLOUCESTER LANDFILL

H. Whittaker	EETD
Carolyn I. Adams	Waterloo University
Susan A. Salo	Waterloo University
Andrew Morgan	Algonquin College

Summary

This report describes reverse osmosis (RO) as a method of concentrating dilute organic solutions resulting from chemical spills. The results of a 30 day trial of an RO unit at a chemical landfill are shown and conclusions drawn.

It was concluded that RO is a successful method of concentrating dilute organic solutions and that the permeate to concentrate ratio can be as high as 10:1 without significant decrease in membrane rejection.

Introduction

Recently, reverse osmosis (RO) has been recognized as a useful, low cost separation process with numerous industrial applications. Although originally intended to produce potable water from sea water, improved technology has also made it an effective method for waste treatment. The process involves a semi-permeable membrane which rejects the contaminants in the solution, allowing the solvent to permeate through.

A mobile, self-contained RO unit was built by Memtek Corporation of Nepean, Ontario for the EPS branch of Environment Canada to use in chemical spill cleanup. Since most major rights-of-way in Canada are adjacent to bodies of water large volumes of dilute toxic waste can result from chemical spills. RO would be used to concentrate this water thus reducing the volume which has to be transported for treatment.

Previous studies with the unit have shown that the membranes manufactured by Toray and by Desalination Inc. performed the best of the four membranes tested on dilute organic solutions. Successful demonstrations have also been performed on wood preservative spills. The present study was designed to determine the long term ability of RO to concentrate dilute landfill leachate and how much concentration is possible. The test took place at a former chemical waste landfill for 30 days of continuous operation.

The Theory of Reverse Osmosis

The natural process of osmosis occurs when two solutions of different potentials reach equilibrium across a semi-permeable membrane. The solvent flows from the lower to higher concentration. Figure 1A illustrates osmosis.

In reverse osmosis pressure is applied to the more concentrated solution to reverse natural flow of the solvent. The applied pressure must be greater than the osmotic pressure of the solution (usually 300-1000 psi). The solvent flows through the membrane while the larger compounds are rejected. This process is shown in Figure 1B.

Although larger molecules tend to have better rejection, RO is not separation based on size. The actual mechanism of RO membranes has not been defined but it is known to depend on the chemical structure of the membrane; the chemical and physical nature of the component and experimental conditions as well as the porous nature of the membrane. There are no phase changes during separation by RO. The permeate exits at atmospheric temperature and pressure while the concentrate is removed through a control valve. RO works equally well for liquids or for gases. In addition, RO has lower energy consumption than other separation processes.

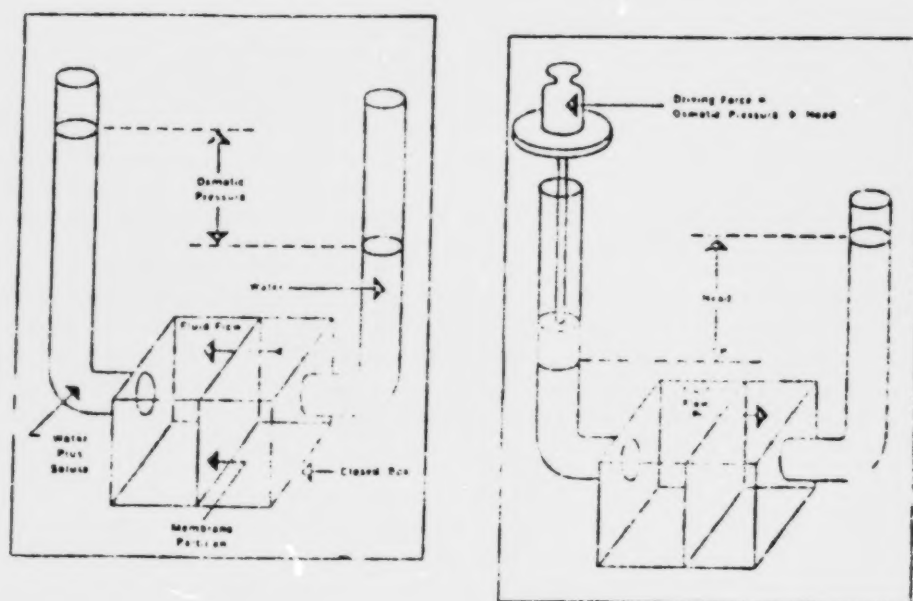


Figure 1: Osmosis and Reverse Osmosis

RO Membranes

New developments in membrane technology have expanded the industrial applications of RO from its original purpose of removing salt from sea water. In the early 1960's Loeb and Sourirajan of UCLA developed a cellulose acetate membrane with an asymmetric density. Its thin dense surface (0.1-1.0 μ m) with thicker porous substructure allowed for higher water flow. Therefore, RO could be used on larger volumes than before. In the late 1970's thin-film composite (TFC) polyamide membranes were introduced. These are made by an aqueous polymeric amine solution layered over a porous polysulphone sub-structure. The TFC membranes are not as susceptible to biological attack and resist hydrolysis.

Both the DSI and Toray membranes used in the trial are TFC spiral wound membranes. The PEC 1000 by Toray is made from TFC Polyether-Polysulphone material while the B441 from Desalination Inc. uses TFC Polyamide. In spiral wound membranes (Figure 2) two flat films are joined by a tricot permeate channel cloth and wound around a plastic tube. The feed enters at one end, parallel to the membranes and the concentrate exists at the opposite end. The permeate escapes through the plastic tube via the tricot cloth. Other types of membranes available are the hollow fiber and tubular membranes.

Pretreatment of the feed water is usually necessary to prevent clogging of the membranes. Problems can arise from suspended solids, bacterial growth on membranes, calcium carbonate or silica build-up and hydrolysis from acidic or alkali water. Filtration will remove suspended solids; the bacteria can be prevented with sodium hexametaphosphate and acid can be added to remove calcium carbonate and to maintain the pH between 5-6 to prevent hydrolysis.

The EPS RO Unit

The EPS mobile reverse osmosis unit was originally conceived as a mobile source of fresh water for the Coast Guard in Newfoundland. Its objective was altered during design to include the capability to concentrate dilute solutions resulting from chemical spills along transportation routes.

Specification of the RO Unit

The self-contained RO unit (Figure 4) designed by Memtek Corp., is powered by a Lister ST3 aircooled diesel engine with a 60.5 L fuel tank - sufficient for ten hours operation. The unit's layout is shown in Figure 1 along with the schematic RO operation (Figure 5). It can be transported by helicopter or by a car with a trailer hitch. The 1135 kg unit also features electrical generators for unit operation and any necessary lighting. It has a structural steel frame which can withstand a 3 m drop and roll over. It processes a minimum of 1800 L/h of permeate at 25°C through 2 banks of membrane elements (Figure 5). The instrument board can be operated manually or automatically. The automatic controls are fitted to shutdown in the event of:

- 1) normal temperatures and pressures are not met or are exceeded;
- 2) blocked inlet; or
- 3) ruptured membrane (inorganic chemicals only).

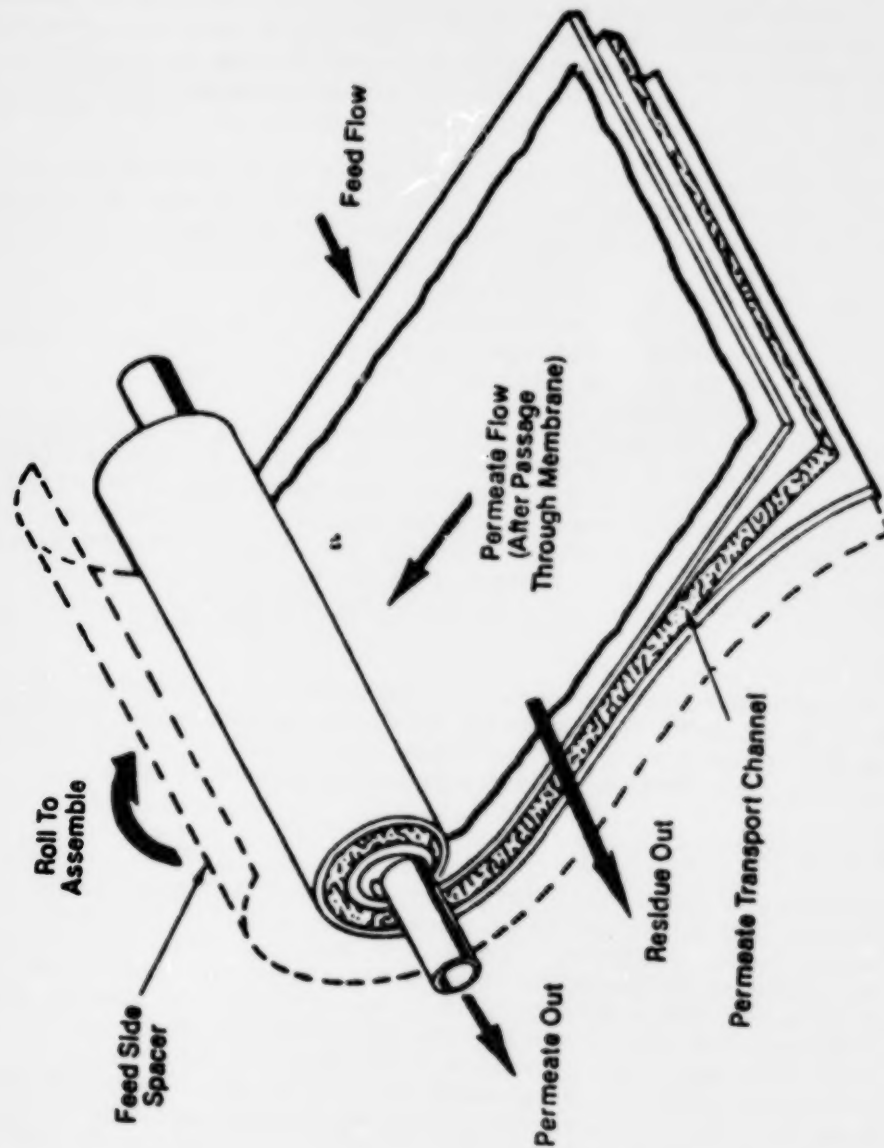


Figure 2: Figure 2. Spiral-Wound Element Construction

Previous Testing

The unit was initially tested in Sept. - Oct. 1983 at the Gloucester landfill site for a 38 hour test on the landfill leachate. At this time four different membranes were tested. The Toray and DSI membranes proved superior. The unit was also tested at the site of two wood preservative spills in Vancouver, B.C. After 180 hours, 99.9 percent of the chlorinated phenols had been removed from the spill water.

The Gloucester Landfill (GLF) Site

The Gloucester landfill site is part of a former municipal landfill which Federal Government labs in the National Capital Region used as a special waste compound for hazardous wastes from 1969 to 1980. During this time 108, 200 L of liquid wastes and 23.8 tonnes of boxed liquid and solid wastes were dumped. The toxic organic contaminants have begun to leach toward local water well supplies via two aquifers (Figure 6). The RO unit was suggested as a possible alternative for concentrating the leachate for cleanup by other processes.

Purpose of the Trial

The GLF trial, which was carried out at well 36W, was meant to demonstrate the ability of RO to concentrate toxic organics in dilute landfill leachate over a long period. The unit was run for 30 24-hour days in order to simulate extended use. In addition the concentrate stream was recycled at various permeate to concentrate ratios (Figure 3) in order to determine if the membrane's rejection deteriorated significantly as the concentration of the feed increased.

As a separate part of the trial, a large proportion of the concentrate was used as feed for physical-chemical processes set up, on pilot plant scale, by Burlington Environmental Technology Centre. The objective was to determine the ability of these processes to treat the concentrate.

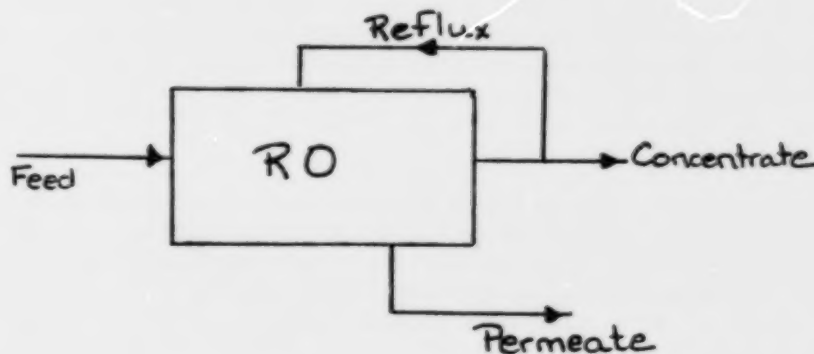


Figure 3: Figure 3. Block Diagram of GLF RO unit trial

Cost of RO

RO is an especially attractive process due to low maintenance and operating costs. If the feed is properly pretreated, the membranes will last for several years. The hardware of a unit consists of simple, familiar parts such as pumps, motors, valves, flowmeters and pressure gauges which are easily operated and repaired. The unit can be automated to reduce labour costs as well. The portable unit runs on diesel fuel (6 L/h) while a stationary model would run on electricity.

Initial costs of a unit and membranes depend on size and type. A mobile unit costs approximately \$60,000 while stationary models range from \$15,000 to \$50,000 or more depending on the capacity. Membranes vary considerably in price with the DSI selling at \$915 and the Toray at \$360 for a 100 cm by 10 cm membrane. Operating costs can be further reduced by recycling either the permeate of the concentrate or both.

Methods of Analysis

The organic compounds were determined, by the purge and trap method, on the Hewlett Packard model 5830A Gas Chromatograph. A 5 ml sample was consistently used so that sample concentration would be linearly related to the area of the peaks in the chromatograph. The linear relationship was determined by a series of standards of different concentrations. The concentration of the feed and the concentrate is shown in Table 3. The percent rejection of each compound is shown in Table 4 and 5.

The cations were analysed on an atomic absorption spectrometer. The 4:1 ratio was done on the IL 251 AA but mechanical difficulties necessitated that the analysis be completed on the Perkin-Elmer model 460. The anions were determined by a Ion Exchange Chromatography on the Dionex. The results of this analysis is shown in Table 4.

Results

Organic Compounds

In excess of 1.7 million litres of leachate were processed by RO during the trial. Although the RO unit always pumped from the same well, the concentration of the feed shows a steady decrease for all compounds with sporadic fluctuations for some (Table 3). The decrease results from the dilution of the feed by the more pure water which is pumped in from the edges of the aquifer. The fluctuations were probably the result of the widely varying concentration of chemicals found in the leachate. Table 1 details the change in concentration with depth for several compounds of interest at two nearby test wells.

The slight rise in the concentration of the feed at the 8:1 ratio can be attributed to a 36-hour shutdown after the 6:1 ratio. During this time, water flowed away more quickly than the volatile organic compounds. The feed became more concentrated but was once again diluted when pumping restarted. Small pockets of more concentrated compounds occur throughout the aquifer where certain chemicals have been dumped in more concentrated amounts. Since many of the organics are not very soluble in water they do not disperse equally throughout the aquifer. This can be seen in the data for the co-eluting compounds; 1,1,1-trichloroethane and 1,4-dioxane. Fl for the 6:1 ratio is substantially higher than any of the other surrounding readings.

The occasional sharp decreases in feed concentration probably are due to air stripping within the lines caused by a leak. The air stripped feeds will also have lower individual rejections since some of the volatile organics have been stripped and do not show in the feed sample. These compounds will, however, be forced back into solution by the high pressure pumps and will be at least partially detectable in the permeate and concentrate. For more easily air stripped compounds there are more contaminants in the permeate than in the feed. An example of the air stripping can be seen in the F2 stream of the 6:1 ratio. This problem is compounded by the widely varying concentrations in the leachate.

The percent rejection figures shown in Table 4 seem to indicate that RO begins to fail at the higher concentrations. However, upon looking at daily percent rejections, the decrease is gradual, there are no large decreases at the change in ratios. The lower percent rejections can be attributed mainly to a single membrane. A leak in one pressure vessel was noted and corrected during the 5:1 ratio. An increase in the percent rejection is noticed in the 6:1 ratio as a result. However one membrane vessel consistently showed lower rejections when individual permeate streams were tested. It can therefore be concluded that the drop in percent rejection is due mainly to faulty membranes, and not to the inability of RO to handle greater concentrations.

It should be noted that the faulty DSI membrane bank had been previously used at the wood preservative spill in B.C. All other membranes were new.

The Toray membrane showed almost no change in concentration of chemicals in the permeate throughout the trial.

Inorganic Compounds

The inorganics do not follow the same trends as the organics. The inorganic feed is constant - it does not decrease with pumping. Since the inorganic compounds are more soluble in water they diffuse evenly throughout the aquifer; therefore the diluting effect is not noticed.

Only the chlorine anion was present in large enough quantities to detect on the Dionex. Rejection was usually greater than 98 percent. The 5:1 and 10:1 ratios were 95.03 percent and 93.63 percent respectively. The leaking membrane is most likely the cause for this decrease.

The cations show more variety than the anions. Sodium and potassium are much lower than expected but due to the rejection of the chlorine ion this is most likely due to ionic interferences in the AA measurements. Removals were above 95 percent for calcium, magnesium and manganese.

Conclusions

RO is a successful method for concentrating dilute organic solutions. The reflux ratio can be as high as 10:1 without major differences in percent rejection. However, membranes wear out much more quickly than specified when used on other than saline solutions. The membrane which had previously been used on wood preservative caused trouble during the trial.

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TABLE 1

VARIATION OF CHEMICAL CONCENTRATION WITH DEPTH AT WELLS 16M and 37M (Reference 4)

DEPTH (Metres)	ACETONE		1,1 DICHLOROETHANE/THF		CHLOROFORM/DIETHYL ETHER		TRICHLOROETHANE		BENZENE	
	16M	37M	16M	37M	16M	37M	16M	37M	16M	37M
1	N/D	N/D	N/D	2	2	59	N/D	24	N/D	71
2	N/D	N/D	TRACE	TRACE	1	83	TRACE	30	N/D	94
3	N/D	N/D	N/D	9	TRACE	220	TRACE	31	N/D	115
4	N/D	N/D	N/D	31	N/D	665	TRACE	34	N/D	128
5	N/D	490	N/D	375	TRACE	3430	1	24	N/D	1140
6	N/D	N/D	N/D	1	1	3491	1	26	N/D	1540
7	N/D	2030	TRACE	730	29	7940	TRACE	27	N/D	2950
8	N/D	9370	TRACE	1310	N/D	53200	TRACE	32	N/D	10300
9	N/D	13700	35	1980	100	33900	5	35	2	14700
10	N/D	890	37	190	80	1875	7	13	3	766
11	10	1210	124	1100	330	10040	170	250	53	4120
12	120	905	555	1230	1450	2240	164	83	150	2890
13	1510	630	1242	1195	3125	3270	11	460	40	2860
14	320	400	87	1020	620	1570	108	202	33	3197
15	1950	1120	264	33	3850	135	580	134	200	646
16	330	1250	6	30	640	4540	100	740	38	164

TABLE 2

ORGANIC COMPOUNDS ANALYSED

The following is the list of organic compounds analysed.
These chemicals will be referred to by number in future tables.

1. Acetone
2. 1,1-dichloroethane/THF
3. Chloroform
4. Diethyl ether
5. 1,2,-dichloroethane
6. 1,1,1-trichloroethane/1,4-dioxane
7. Trichloroethane
8. Benzene

TABLE 3

CONCENTRATION OF ORGANICS IN FEED AND CONCENTRATE STREAMS (in ppb)

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
4:1 Ratio							
F1	13600	166	3450	27.1	66.3	57.7	26.7
F2	14300	186	6110	37.1	111	65.2	44.8
F3	12500	163	5960	33.0	107	51.0	37.3
C avg	67200	964	26400	1710	473	311	177
5:1 Ratio							
F1	7100	84.9	1530	24.3	68.8	400	12.5
F2	9000	120	4680	22.7	94.7	44.3	32.9
F3	9000	123	4880	22.6	97.6	45.3	35.4
C avg	54100	816	18200	1630	487	2450	147
6:1 Ratio							
F1	6800	87.2	2650	188	84.9	492	26.0
F2	1900	22.8	660	48.4	20.7	69.5	5.66
F3	7100	119	4600	192	93.5	48.3	36.8
C avg	49200	964	23200	1580	499	1460	181
8:1 Ratio							
F1	6200	105	4160	164	81.2	51.2	31.7
F2	3500	77.6	3050	106	68.6	112	34.4
F3	3300	76.7	3010	101	68.7	87.8	34.8
C avg	27000	646	12900	1110	368	2070	124
10:1 Ratio							
F1	2000	54.7	1990	58.7	43.8	43.5	23.4
F2	2400	70.5	2310	77.4	56.9	37.1	31.3
F3	2900	69.8	2700	92.0	74.8	59.3	31.8
C avg	14000	535	11400	709	270	675	125

202
TABLE 4

AVERAGE CONCENTRATION (in ppm) OF INORGANICS IN FEED
AND CONCENTRATE STREAMS

<u>COMPOUND</u>		<u>4:1</u>	<u>5:1</u>	<u>6:1</u>	<u>8:1</u>	<u>10:1</u>
Calcium	F:	114	70.5	69.2	77.4	71.6
	C:	446	516	455	761	864
Magnesium	F:	40.7	30.0	28.7	28.8	28.1
	C:	118	206	212	303	236
Sodium	F:	6.34	8.78	8.93	8.44	8.48
	C:	45.8	62.0	81.3	146	72.8
Potassium	F:	1.20	1.02	0.95	0.89	0.93
	C:	5.66	5.63	6.20	7.60	7.33
Manganese	F:	0.53	0.56	0.60	0.60	0.60
	C:	1.34	3.46	2.90	5.74	6.60
Chlorine	F:	84.6	95.6	90.6	98.9	150
	C:	429	738	643	778	1220

TABLE 5

AVERAGE PERCENT REMOVAL FOR ORGANIC COMPOUNDS

Calculation: $(1-P/F) \times 100$

<u>COMPOUND</u>	<u>4:1</u>	<u>5:1</u>	<u>6:1</u>	<u>8:1</u>	<u>10:1</u>
1	84.6	70.0	74.2	65.1	67.3
2	95.5	90.3	94.0	87.1	85.3
3	92.5	85.7	88.4	83.2	77.2
4	95.3	90.7	93.9	88.1	85.5
5	84.4	70.4	73.9	68.3	57.6
6	90.0	86.6	98.2	96.4	86.6
7	86.4	75.0	82.2	76.9	62.4
8	94.1	87.8	93.9	89.9	83.1
TOTAL	91.1	83.1	87.6	82.1	77.1

TABLE 6

AVERAGE PERCENT REMOVAL FOR INORGANIC COMPOUNDS

<u>COMPOUND</u>	<u>4:1</u>	<u>5:1</u>	<u>6:1</u>	<u>8:1</u>	<u>10:1</u>
Calcium	97.5	94.4	97.7	94.9	93.5
Magnesium	N/A	94.9	97.3	96.8	96.3
Sodium	72.6	76.0	77.1	74.0	74.1
Potassium	80.6	61.7	70.6	69.1	60.2
Manganese	99.9	99.9	99.9	99.9	99.9
Chlorine	99.9	95.0	99.0	98.0	93.6

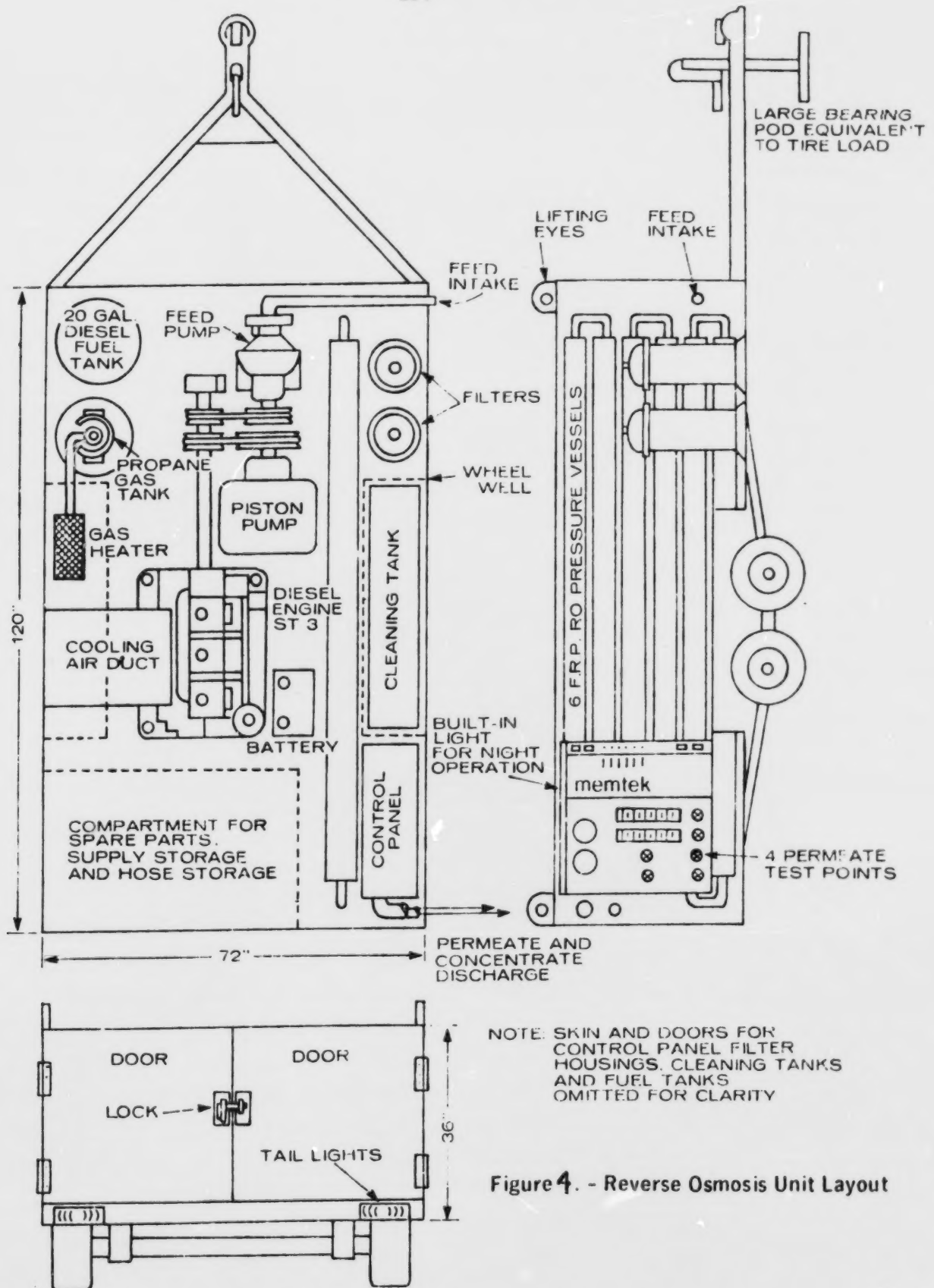


Figure 4. - Reverse Osmosis Unit Layout

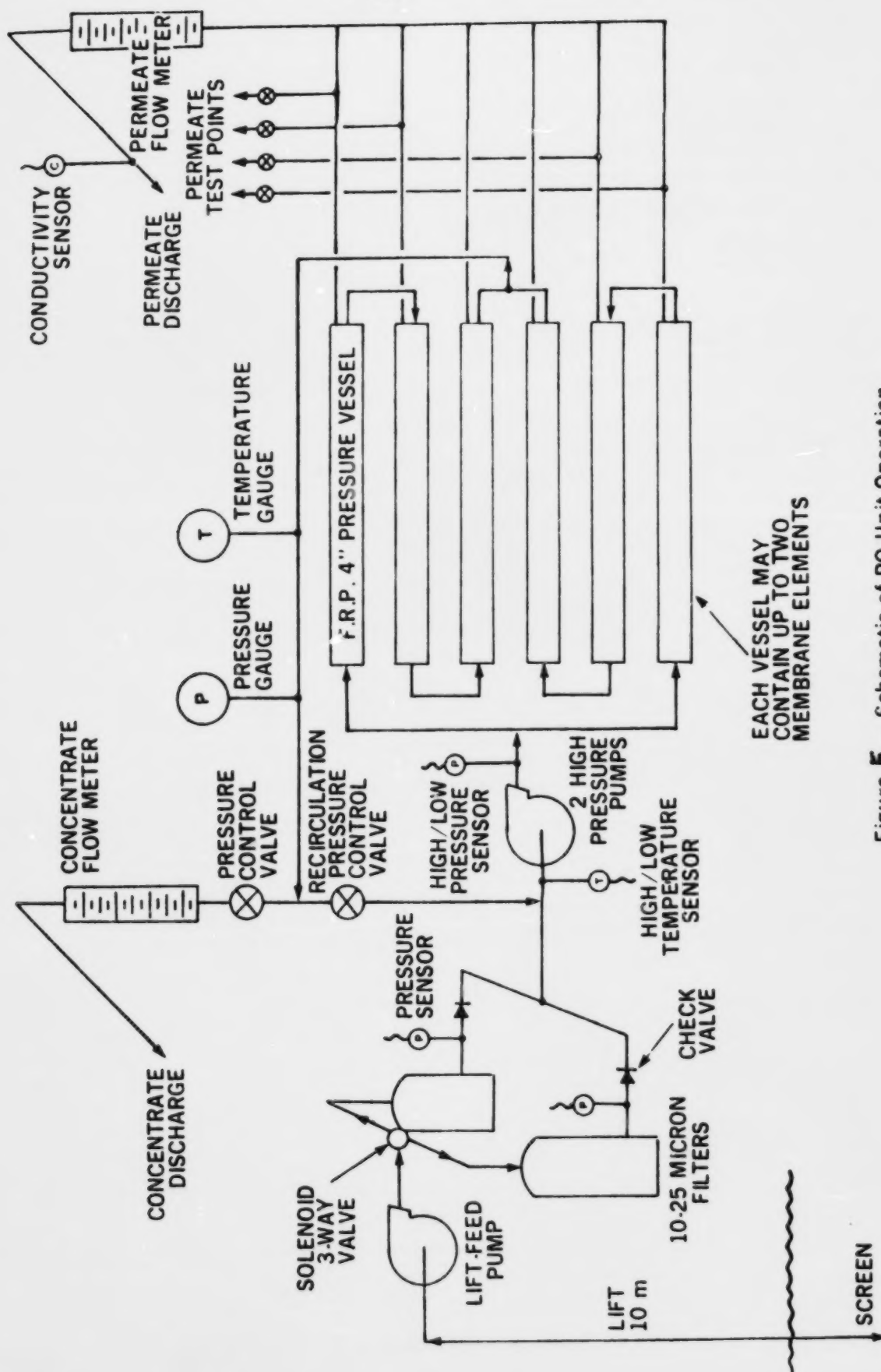
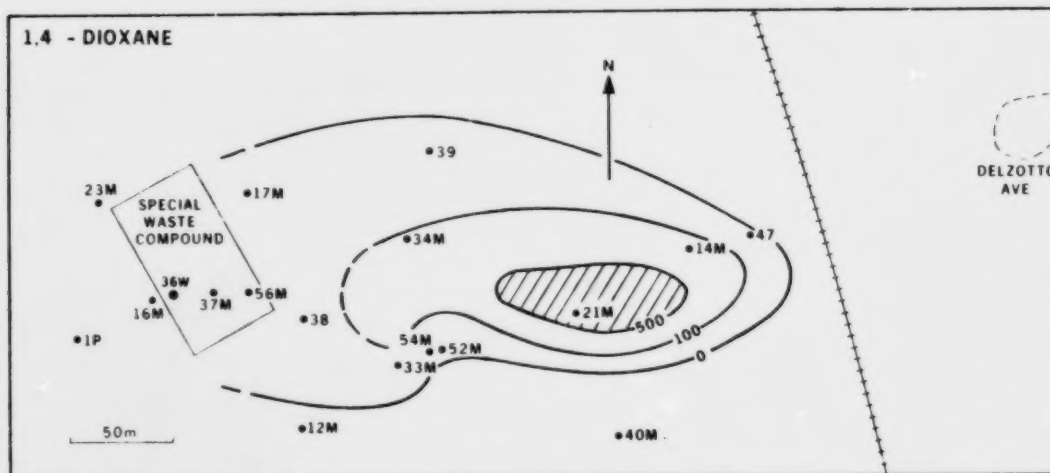
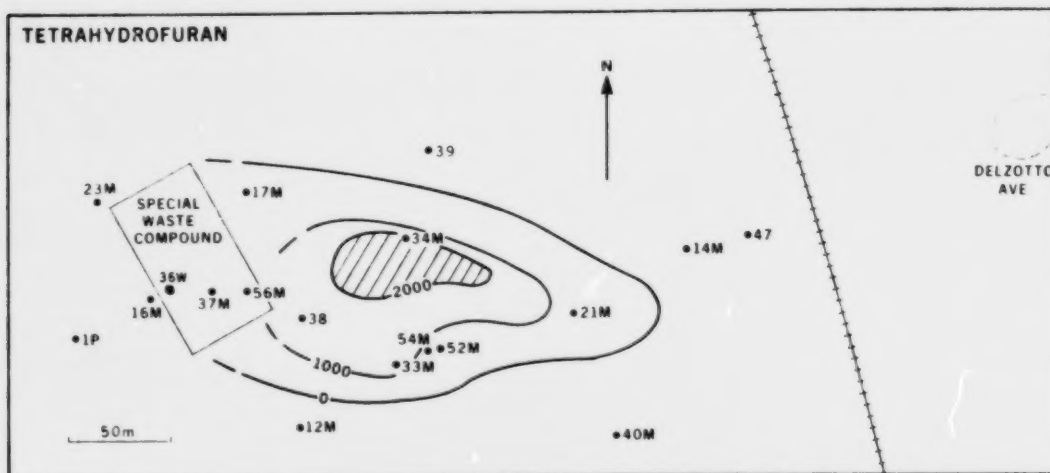
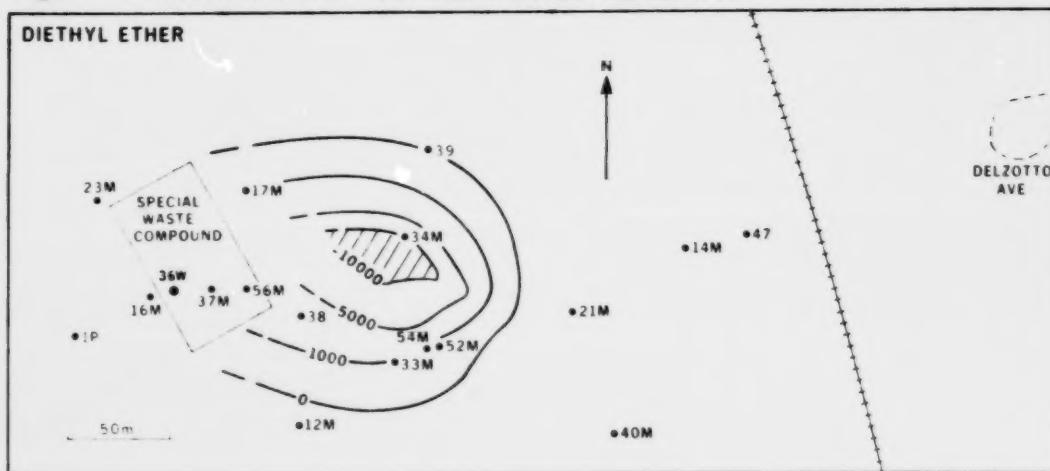


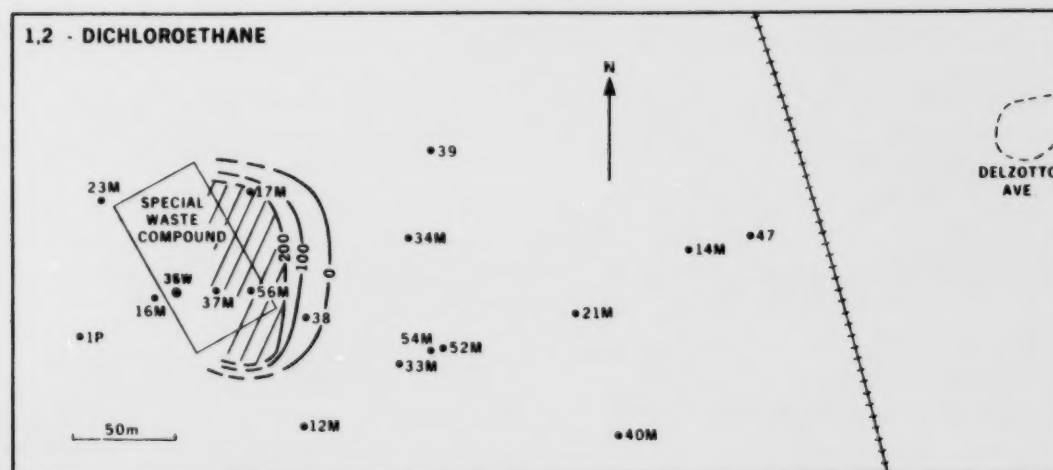
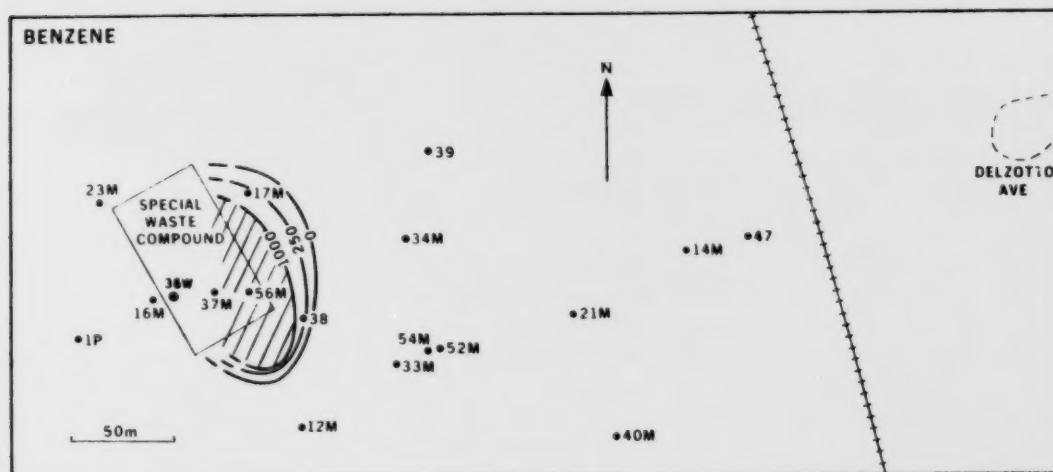
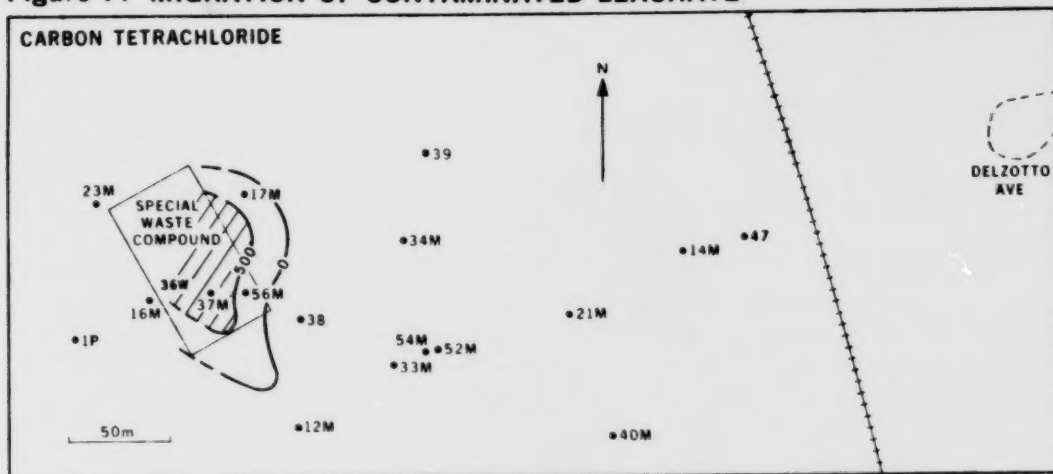
Figure 5 - Schematic of RO Unit Operation

Figure 6. MIGRATION OF CONTAMINATED LEACHATE

**LEGEND**

- MULTILEVEL SAMPLER OR PIEZOMETER
- 500- CONTOUR OF MAXIMUM CONCENTRATION (PARTS PER BILLION) ENCOUNTERED IN SECTION (1982)
- AREA OF MAXIMUM CONCENTRATION

Figure 7. MIGRATION OF CONTAMINATED LEACHATE

**LEGEND**

- MULTILEVEL SAMPLER OR PIEZOMETER
- 500— CONTOUR OF MAXIMUM CONCENTRATION (PARTS PER BILLION) ENCOUNTERED IN SECTION (1982)
- AREA OF MAXIMUM CONCENTRATION

A STUDY OF VAPOUR SPILL CONTROL TECHNOLOGY

I.A. Buist, P.Eng. and L.B. Solsberg*, P.Eng.
S.L. Ross Environmental Research Limited
Ottawa, Ontario

INTRODUCTION

An engineering assessment was undertaken, on behalf of the Environmental Protection Service, by S.L. Ross Environmental Research Limited and Concord Scientific Corporation, of existing technologies with potential applicability to control the vapour or gas component of spilled chemicals and liquefied gases. The study was initiated largely because a survey previously undertaken for EPS of chemical countermeasures revealed vapour spill control to be the response option most noticeably lacking in respect to an EPS list of priority substances. In fact, a list of 33 priority substances was provided as a focal point for evaluating various spill control technologies in this study. These were:

Gases Lighter Than Air:Less or Insoluble in WaterFlammable

Acetylene
Ethylene
Hydrogen gas
Natural gas
Petroleum gas

Gases Heavier Than Air:Less or Insoluble in WaterFlammable

Acrylonitrile (vapours)
Benzene (vapours)
Butylene
Carbon Disulfide (vapours)
Dimethyl Ether
Hydrogen Sulfide
Propylene
Vinyl Chloride
1,3 - Butadiene

Less Flammable

Arsine
Carbon Dioxide
Carbon Tetrachloride (vapours)
Chlorine
Chloroform (vapours)
Fluorochloromethanes

Soluble in Water:Flammable

Acetaldehyde (vapours)
Acetic Acid (vapours)
Ethylene Oxide
Formaldehyde (gas)
Hydrazine (vapours)
Methylamines
Propylene Oxide (vapours)

Less Flammable

Anhydrous Ammonia
Formic Acid (vapours)
Hydrogen Chloride
Hydrogen Fluoride
Sulfur Dioxide
Sulfuric Acid (vapours)

*presently with Hatfield Consultants Limited, West Vancouver, B.C.

It was specified that the following concepts were to be examined:

- 1) adapted air pollution equipment (aqueous packed column, tank of reactant material, absorbent bed) combined with a tubing device reaching the leak;
- 2) a vacuum system (e.g. vacuum truck) combined with a scrubbing system; a Porta-tank and solvents; cement mixer truck and treating or neutralizing agents;
- 3) a vapour compression evaporation system combined with a scrubbing system;
- 4) use of a ring of fire to create a dispersive updraft; and
- 5) use of a small safety burner for the combustion of flammable gases (hazards of the combustion products to be considered).

Exceptions noted for omission from the study included foams, gelling agents, cooling agents, cloth or particulate covers and surfactant films.

Spill conditions to be considered during this investigation were to include:

- small releases for which plugging and transferring to another container could not be accomplished;
- vapours generated from a pool of chemical sufficiently deep so as to allow a response time of some hours; and
- gases and vapour clouds lying near the ground.

The attachment of ducts or hoses to a leaking container was not to be addressed.

CHEMICAL CLASSIFICATION

The physical and chemical properties of the 33 chemicals of concern were compiled initially since these are major factors determining the fate and behaviour of the spill as well as applicable amelioration methods. Similarly, a summary of information on their transportation (size of container and physical state in container) was also prepared. Three behavioural groups were then identified which could be used to generally characterize possible spill situations. As part of this preliminary work, chemical reactions were also studied which the released vapours or gases might undergo.

The three categories of chemicals or behavioural groups were differentiated according to their physical state after being spilled:

- A) Liquids at ambient temperature (-10 to 25°C) and atmospheric pressure.
- B) Lighter than air gases at ambient temperature and pressure.
- C) Heavier than air vapours at ambient temperature and pressure.

In Category A - liquids, the spilled material can exist as a pool from which vapours are emitted. Substances in this category therefore include liquids with relatively high boiling points and lower vapour pressure, and would be transported in the liquid state under ambient temperature and pressure.

Substances in Categories B and C exist as gases or vapours and, under ambient conditions, would not be in equilibrium with a liquid pool. These substances however, may be transported in a liquefied state by virtue of pressurization and/or cooling.

The classification of the substances into these three groups is given in Table 1. Note that three substances (acetaldehyde, ethylene oxide and hydrogen fluoride) appear in each of two categories since their boiling points fall within the range of ambient temperatures for the study (-10 to 25°C). These substances may exist as either a liquid or a vapour, depending on the ambient temperature. Also indicated in Table 1 is the state in which each substance is transported.

SPILL SCENARIOS

The potential spill situations were then described in terms of accident scenarios for eight chemicals representative of various behavioural groups. It was assumed that the spill would occur over a period of three to twenty-four hours. This period was selected as a reasonable time span over which vapour response might be feasible or necessary. Given this spill or leak duration, rough estimates of the release rates and nominal hole sizes were estimated for railway cars, which comprise typical containers.

In the case of liquids, pool sizes corresponding to a maximum value dependent on the discharge rate from the tank and the evaporation rate from the pool were calculated. This maximum pool size is independent of the pool depth; however, the minimum time required to obtain the maximum pool area can be calculated by assuming a pool depth. As an illustrative example, the time required to obtain a 10 cm deep pool of maximum area was calculated for propylene oxide. For liquids, the release of liquid below the liquid level and of vapour above the liquid level was considered.

The disposition of the gas or vapour cloud is of concern for potential treatment and also for assessing safety of personnel and equipment. In particular, the zones within which the threshold limiting value (TLV)* and/or the lower flammability limit (LFL) are exceeded, were calculated where possible.

The dispersion characteristics at distances less than 0.1 km are not considered reliable. The safety parameters were selected (TLV or LFL) so that the zone defined was the smallest-consistent with the validity of applying the dispersion calculation.

In the case of gases, both lighter or denser than air, the nature of their release depends on the physical state in which they are transported. For substances transported as liquids - by virtue of pressurization and/or cooling releases from above and below the liquid level were considered. For light or dense gases transported as compressed gases, only one type of release is possible.

Spill scenarios for representatives of each of the three classes or behavioural groups are described below:

Liquids

The group of designated liquids has a wide range of vapour pressures (or boiling points) - from acetic acid with 2.0 kPa and benzene with 12.7 kPa, to propylene oxide with 85 kPa at 25°C. Both benzene and acetic acid have boiling points well above the range of ambient temperatures. On the other hand, propylene oxide with a boiling point of 23.2°C, has the potential to be at its boiling point under some atmospheric conditions. These three liquids therefore formed the basis for spill scenarios representing liquids covering the entire range of vapour pressures.

*Recent discussion suggests that 10 times the TLV is a more accurate representative of limiting concentrations for emergency situations. Nevertheless, to be conservative the published TLV was used in this study.

TABLE I

Classification of Chemicals Based on
Physical State at Ambient Conditions

Category A Liquids	Category B Light Gases	Category C Dense Vapours
Sulphuric Acid (310°C)*	Acetylene (0.908, g)**	Butylene (1.9, 1)**
Acetic Acid (118°C)	Ethylene (0.975, g)	Dimethylether (1.6, 1)
Hydrazine (113.5°C)	Natural Gas (0.55, 1)	Hydrogen Sulphide (1.2, 1)
Formic Acid (100.7°C)	Anhydrous Ammonia (0.6, 1)	Propylene (1.4, 1)
Benzene (80.1°C)	Hydrogen (0.67, g)	Vinyl Chloride (2.2, 1)
Acrylonitrile (77.4°C)		1-3 Butadiene (1.9, 1)
Carbon Tetrachloride (76.5°C)		Arsine (2.7, g)
Formaldehyde (97°C)		Carbon Dioxide (2.6, g&l)
Chloroform (61.7°C)		Chlorine (2.4, 1)
Carbon disulphide (46.3°C)		Fluorochloromethanes (4.2, 1)
Propylene Oxide (34.3°C)		Acetaldehyde (1.5, 1)
Acetaldehyde (20.8°C)		Ethylene Oxide (1.5, 1)
Hydrogen fluoride (19.5°C)		Petroleum Gas (1.5, 1)
Ethylene Oxide (13.5°C)		Methylamines (1.1, 1)
		Hydrogen Chloride (1.3, 1)
		Hydrogen Fluoride (2.1, 1)
		Sulphur Dioxide (2.26, 1)

* Normal boiling points.

** Relative density of vapour at 25° and transportation phase.

Light Gases

This group contains five gases all with relative densities less than one. These gases may be transported as a gas or as a compressed liquid. Anhydrous ammonia is representative of this category. Compounds in this category stored or transported as gas will exhibit similar plume-type dispersion.

Ammonia presents a special problem; although lighter than air, it tends to form heavier-than-air clouds or puffs when spilled under some spill conditions. The scenario for ammonia was constructed to cover two of the possible types of spills from this compound category.

Gases transported as pressurized or chilled liquids in this category can also be represented by the propylene spill scenarios (see below). Although propylene is heavier than air, the density difference is small and pockets of gas are not likely to form unless wind speed is negligible.

Dense Vapours

The compounds in this category are all heavier than air and may be transported as liquefied or compressed gas. Scenarios were described for two compounds representing near extremes of the range of densities of gases in this category which are transported in the liquefied state. One scenario for a gas transported in the gaseous state was also described.

Propylene, a medium density vapour at ambient temperatures and pressures, and chlorine, an extremely dense gas transported as a liquid, were the examples selected. Chlorine presents a special case in which vapour pockets may stay close to the ground (depending on local topography) causing deviations from predicted plume dispersion. Both propylene and chlorine are transported as liquids. Arsine, an extremely toxic compound was used to represent compounds transported as a gas. The spill scenario prepared for arsine differs from the other scenarios presented because of the transport volume used. A cylinder-type spill was reviewed and hazard zones found to be significant.

Table 2 summarizes the spill scenarios that were developed.

COUNTERMEASURES APPLICABILITY

The applicability of various countermeasures to releases of the thirty-three priority chemicals was assessed on the basis of the substance's physical and chemical properties. These were related to the following unit operations to determine preliminary feasibility in conjunction with the release scenarios:

- enhanced dispersion (dilution)
- combustion
- condensation/liquefaction
- compression
- absorption
- adsorption

Table 3 lists the relevant properties of the chemicals of concern. The selected properties, with reference to their applicability to the above unit operations are:

- boiling point (condensation)
- vapour specific gravity (enhanced dispersion)
- flammability limits (combustion and process safety)
- specific heat (condensation and other heat transfer applications)
- solubility in water (absorption and scrubbing)
- heat of vaporization (condensation and liquefaction)
- other solvents (absorption and scrubbing)
- vapour pressure (compression/liquefaction)
- adsorptivity (removal by activated carbon)

Table 2
Spill Scenario Summary

Category	Transport Phase	Representative Compound	Spill Time (h)	Container	Hole Size (in)	Hole Diameter or Puff Quantity	Max. Evaporation or Vapor Release Rate (lb/s)	Type of Dispersion	Hazard Zones (km)			
									Stability Class F		Stability Class D	
									TLV	LEL	TLV	LEL
Liquid	Liquid (low boiling point)	Propylene Oxide	3	roll	95	27.4 m R, 1 m	5780	R	7.4	0.2	2.4	<0.1
			24		34		720	R	1.8	<0.1	0.7	<0.1
Liquid	Liquid (medium boiling point)	Benzene	3	roll	95	53 m 18.7 m	6171	R	11.7	<0.1	3.2	<0.1
			24		34		770	R	2.8	<0.1	0.9	<0.1
Liquid	Liquid (high boiling point)	Acetic Acid	3	roll	95	171 m 60.5 m	7160	R	14	<0.1	3.3	<0.1
			24		34		970	R	3.7	<0.1	0.9	<0.1
Dense Gas	Liquid	Propylene	3	roll	48	n/a ²	4206	R	0.1	0.1	<0.1	<0.1
			24		16	n/a	575	R	<0.1	<0.1	<0.1	<0.1
Dense Gas	Liquid	Chlorine	<0.1	roll	catastrophic	117600 kg	n/a	P	30 (111 min)	n/a	8.5x3.6 (12 min)	n/a
Dense Gas	Gas	Arsine	<0.1	Cylinder	catastrophic	450 g	n/a	P	8.5 (31.5 min)	n/a	3 (11 min)	n/a
Light Gas	Liquid	Ammonia	3	roll	180	n/a	4030	R	24	<0.1	6.4	<0.1
			<0.1		catastrophic	n/a	n/a	P	100	1.5 x 2.3 ³ m/s x 7.94 ³ (14.2 min) (5.25 h)	3.8 x 4.7 (5 min)	

1 R: plume-rise dispersion, P: puff dispersion

2 Not applicable

3 Plume distance dominated (km) x plume width (km)

TABLE 3
COUNTERMEASURES - RELATED PROPERTIES*

CHEMICAL	T _g (°C)	S.G.v	Flammability Limits (% vol.)	C _p (kJ/mol°C)	ΔH _{vap} (kJ/mol)	GAS/VAPOUR PROPERTY sol. in water (g/100g)	ΔH _{mix} (kJ/mol)	Also Soluble In	Vapour Pressure kPa @ °C	Reactivity on Activated Carbon (% by Weight)
Category A LIQUIDS										
Sulphuric Acid	310	-	N/F	0.16	56	-	-95	-	0	30
Sulphuric Acid (30%)	115	0.4	N/F	0.16	56	-	-95	alcohol, ether, acetone, benzene	2.0 @ 25	30
Acetic Acid	118	2.07	5.4-16	0.068	41.7	-	-11.5	alcohol, benzene	1.9 @ 25	30
Hydrazine	115.5	1.11	4.2-100	0.052	40.1	-	-16.2	alcohol, ether, acetone, benzene	5.5 @ 25	7
Formic Acid	162.7	1.6	18-37	0.044	41.4	-	-2.76	alcohol, ether, acetone, benzene	12.7 @ 25	24
Benzene	80.1	2.7	1.5-7.9	0.135	30.8	0.18	0	alcohol, ether, acetone, benzene	14.5 @ 25	45
Acrylonitrile	76.5	5.3	3.05-17.0	0.064	33.2	0.08	0 small	alcohol, ether, acetone, benzene	1.5 @ 25	0
Carbon Tetrachloride	77.4	1.8	7.0-73	0.088	34.6	0.08	-0.63	alcohol, ether, acetone, benzene	6.3 @ 38	40
Formaldehyde (37%)	97	1.03	N/F	0.035	24.76	0.11	0 small	alcohol, ether, acetone, benzene	28 @ 25	15
Chloroform	61.7	4.1	N/F	0.066	31.4	0.22	-2.47	alcohol, ether	48 @ 25	7
Carbon Disulfide	64.3	2.6	1.5-50	0.037	38.4	0.03	-	alcohol, ether	85 @ 25	13
Propylene Oxide	34.3	2.0	2.1-38.5	0.071	30.5	0.03	-	alcohol, ether, benzene	125 @ 25	7
Acetaldehyde	20.8	1.5	4.0-60	0.033	25.1	-	-	-	-	-
Hydrogen Fluoride	-	-	-	-	-	-	-	-	-	-
Ethylene Oxide	-	-	-	-	-	-	-	-	-	-
Category B GASES										
Acetylene	-80	0.908	2.5-80	0.065	19.5	0.1	0	acetone, benzene	2025 @ -10	2
Ethylene	-103.8	0.975	2.75-28.6	0.0425	13.6	0.015	0	ether	not condensable without chilling	3
Natural Gas	-164	0.55	5.3-14.0	0.035	9.25	2.32	-	alcohol, ether, benzene	not condensable without chilling	0
Ammonia	-33	0.6	15.5-27.0	0.036	23.3	26.8	-13.6	alcohol, ether	640 @ 16	0
Hydrogen	-253	0.067	4-75	0.029	0.892	0.015	-	alcohol	not condensable without chilling	0
Category C DENSE VAPOURS										
Butylene	-6	1.9	1.4-10	0.089	21.9	0	0	alcohol, ether, benzene	275 @ 25	8
Dimethyl Ether	-23	1.6	2-30	0.088	22.6	7.0	small	alcohol, ether, acetone	202 @ -6	10
Hydrogen Sulfide	-60.3	1.2	4.3-45	0.031	18.7	0.46	small	alcohol	1700 @ 20	3
Propylene	-47.3	1.4	2.0-11	0.083	20.9	0	0	alcohol	505 @ -5	5
Vinyl Chloride	-13.4	2.2	4-26	0.055	20.9	0.27	0	alcohol, ether	240 @ 20	0
1-3 Butadiene	-10.9	1.9	2-11.5	0.079	23.6	0.074	0	alcohol, ether, acetone, benzene	202 @ 15	0
Acrolein	-35	2.7	N/F	0.038	16.7	0	0	benzene, carbon test	1515 @ 21	15
Carbon Disulfide	-28	1.23	N/F	0.037	15.4	0.145	-	-	3778 @ 21	0
Chlorine	-35	2.5	N/F	0.034	20.4	0.73	-	alcohol, ether	589 @ 21	15
Fluorochloromethane	-30	4.2	N/F	0.073	35.4	0.028	0	alcohol, ether, acetone, benzene	400 @ -7	5
Ethylene Oxide	-13.5	1.5	3-100%	0.048	28.5	-	-4.25	alcohol, ether, benzene	101 @ 10	0
Petroleum Gas	-42	1.5	2.1-5.5	0.076	11.8	0.006	0	alcohol, ether, benzene	not condensable without chilling	0
Methylamine	-63	1.1	4.3-21	0.052	26.0	-	small	alcohol, ether, acetone, benzene	260 @ 16	10
Hydrogen Chloride	-85	1.5	N/F	0.0295	16.2	50.6	-74.8	alcohol, ether, acetone, benzene	4225 @ 21	10
Hydrogen Fluoride	-19.5	1.3	N/F	0.051	7.49	-	-61.5	alcohol, ether, acetone, benzene	103 @ 20	10
Sulfur Dioxide	-10	2.26	N/F	0.040	23.2	10	-14.0	alcohol, acetic acid	237 @ 21	10

* see Appendix I
Chemical Data Sheets for further information and data sources.

Enhanced Dispersion

Two techniques for reducing airborne concentrations of chemicals were assessed, namely, dilution and raising the contaminant plume to reduce groundlevel concentrations.

The dilution of a gas or vapour stream with air to reduce concentrations to sub-threshold levels was not deemed feasible. Based on the scenarios, the air flowrates required to dilute the escaping gas or vapour to TLV ranged from 23 m³/s (49,000 CFM) for a 920 g/s release of propylene to 2.2×10^5 m³/s for a 4030 g/s release of ammonia. The use of helicopter downwash to flush heavier-than-air vapours from depressions and the use of small fans to clear gases from culverts etc. appear promising for specific spill situations.

The use of a stack or heating to raise a contaminant plume shows promise. Figure 1 shows how a plume of gas or vapour disperses in the presence of a wind. The effect of the ground in reflecting the plume and increasing both groundlevel concentrations and areal extent is also illustrated.

A series of atmospheric dispersion calculations were run on a micro-computer, varying source strength, wind speed, plume rise and atmospheric stability. Figures 2 and 3 compare the results of identical releases, one at ground level and one at 75 m. The higher release point eliminates groundlevel contamination near-source and greatly reduces overall ground-centreline concentrations. It was concluded that a plume rise height of 50 to 75 m would eliminate groundlevel concentrations in excess of the TLV for the thirty-three priority chemicals over the range of release rates investigated.

Three factors contribute to plume rise, stack height, momentum of the gases or vapours and thermal buoyancy. An analysis was undertaken to determine the minimum stack height required to achieve a 75 m plume rise. Figure 4 shows the velocity (or momentum) plume rise achieved by funneling the escaping vapours through a 50 cm diameter ducts as a function of flowrate for various wind speeds. Figure 5 shows the thermal plume rise as a function of heating rate for various wind speeds.

Assuming an average wind speed of 5 m/s, a duct velocity of 20 m/s (a 21.5 KW fan) and a heating rate of 10,000 cal/s (about 3 kg/hr of propane) the stack height need only be 15 to 40 m to achieve a plume rise of 50 to 75 m.

An alternative to this approach is the system proposed by DMSA ACTON Ltd. (Mooney et al, 1980), illustrated in Figure 6. The "Mobile Gas Dispersion System" consists of 12 specially designed propane safety burners placed concentrically around the leaking tank. The thermal updraft created by the burner lifts the plume, thus reducing groundlevel concentrations. Propane would be supplied from a tanker through a control system.

A similar, fixed system has been successfully demonstrated at Canadian chemical process plants.

Combustion

Twenty-three of the 33 priority chemicals are flammable. This suggests that the use of a portable burner or flare stack is a promising vapour spill control technique. Essential elements of a burner include a device for mixing fuel and air in proportions within the limits of flammability and a source of ignition. There are two basic types of gaseous fuel burners, premix and nozzle mix. In the former, air and fuel are mixed in an internal chamber prior to ignition while in the latter fuel is injected into a body of air and ignited; oxygen is provided either by diffusion or mechanical mixing.

FIGURE 1
SCHEMATIC REPRESENTATION OF AIR CONTAMINANT
PLUME DISPERSION MODEL

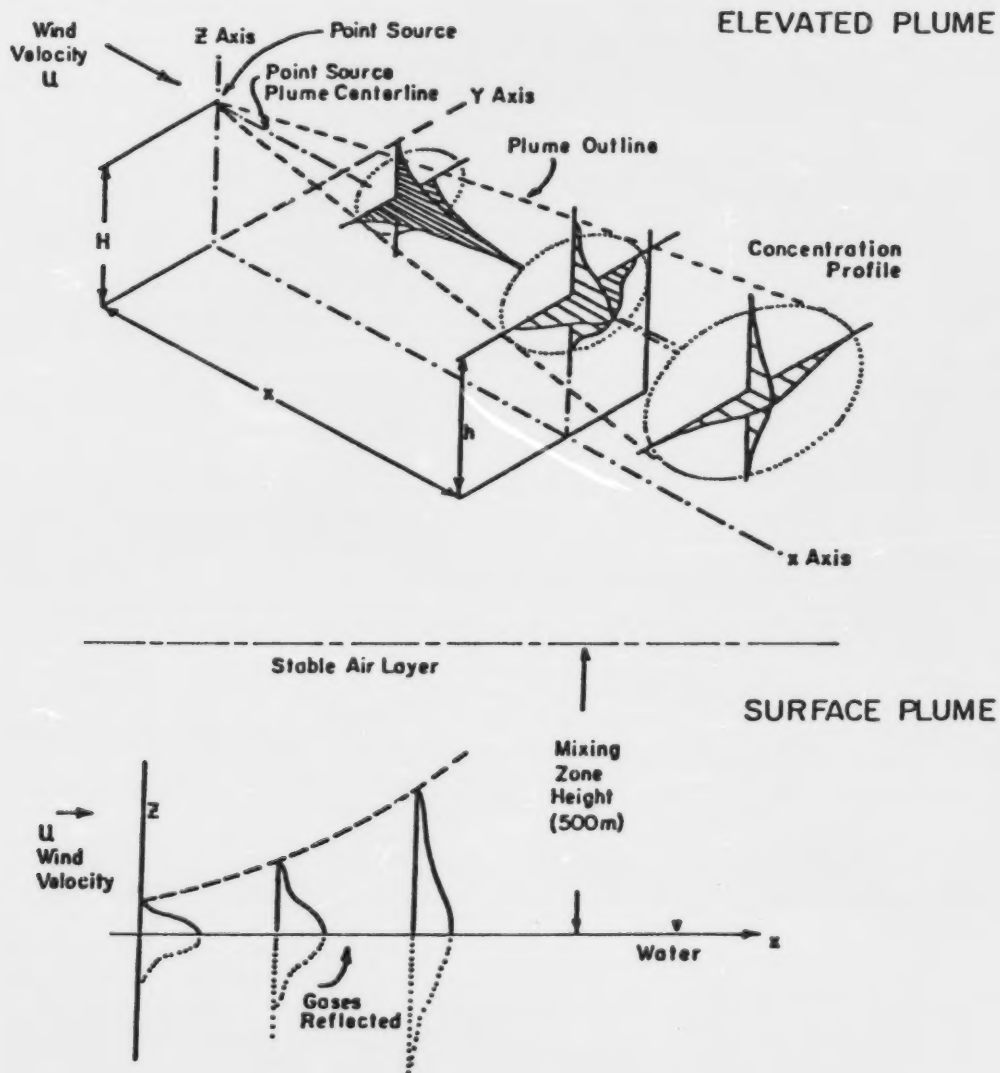


FIGURE 2 EFFECT OF RELEASE HEIGHT ON PLUME DISPERSION

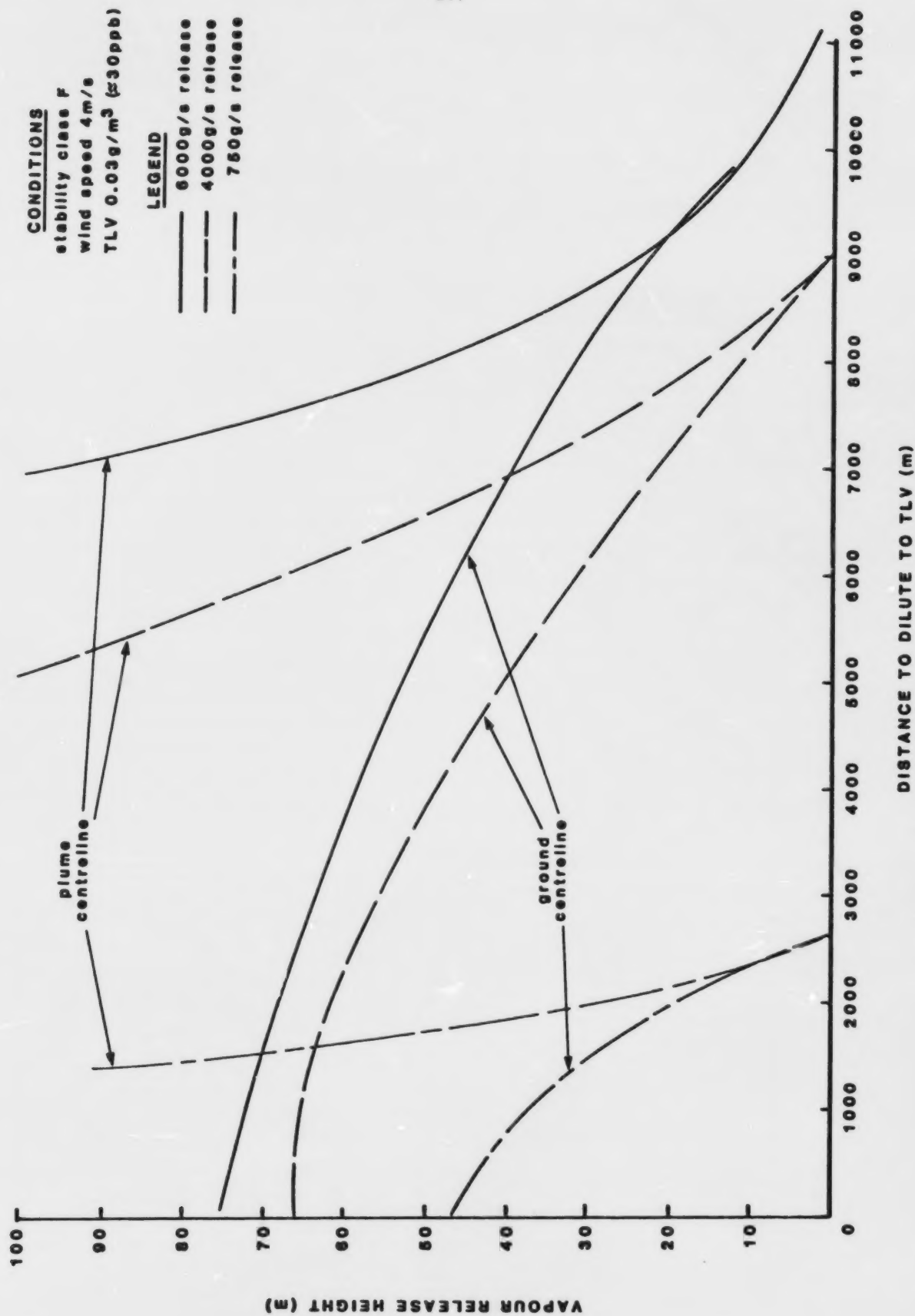


FIGURE 3 VAPOUR CONCENTRATION ISOPLETHS 75m HIGH RELEASE

0000 g/s release
stability class F

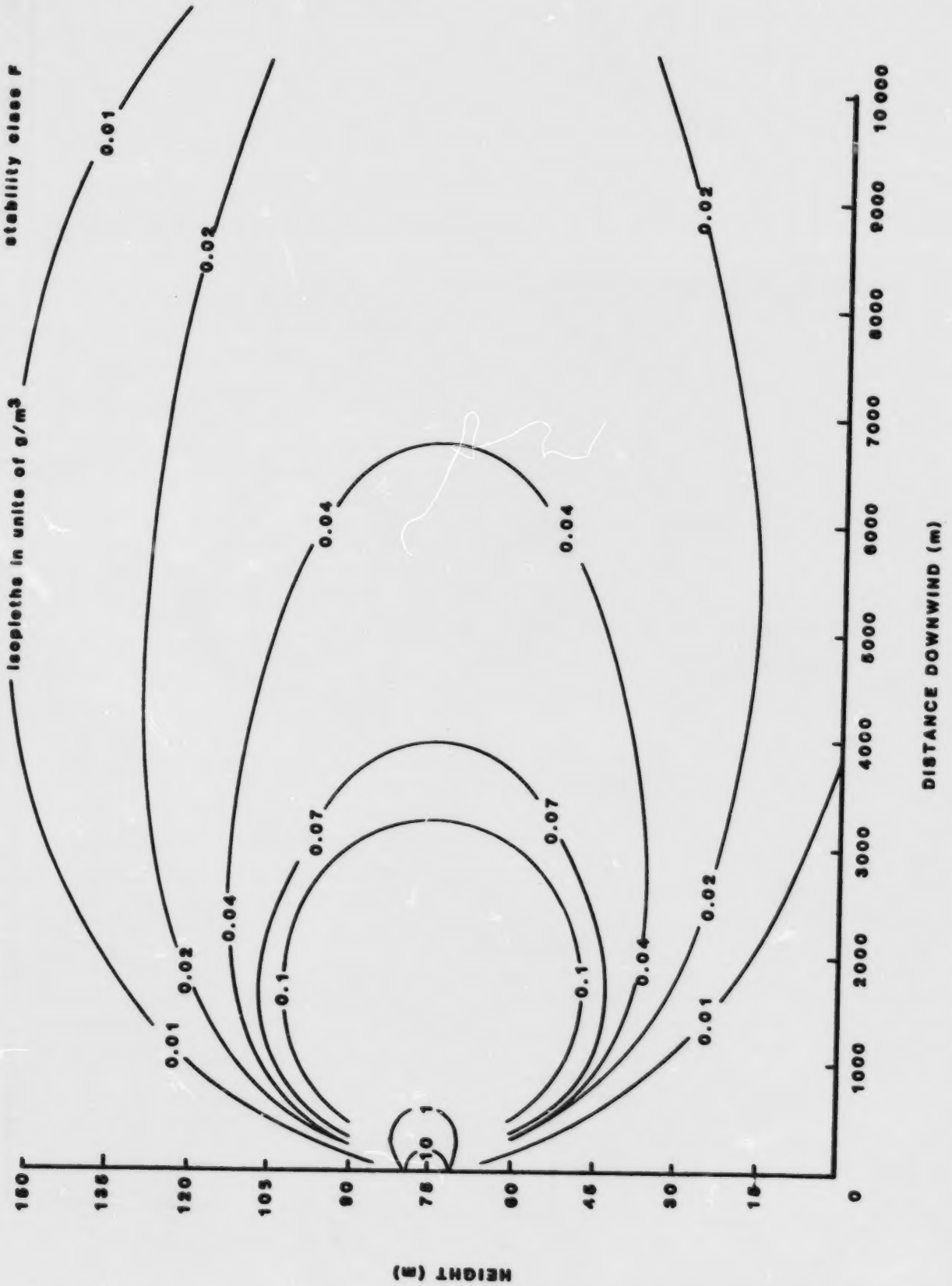


FIGURE 4 VELOCITY PLUME RISE (50cm stack)

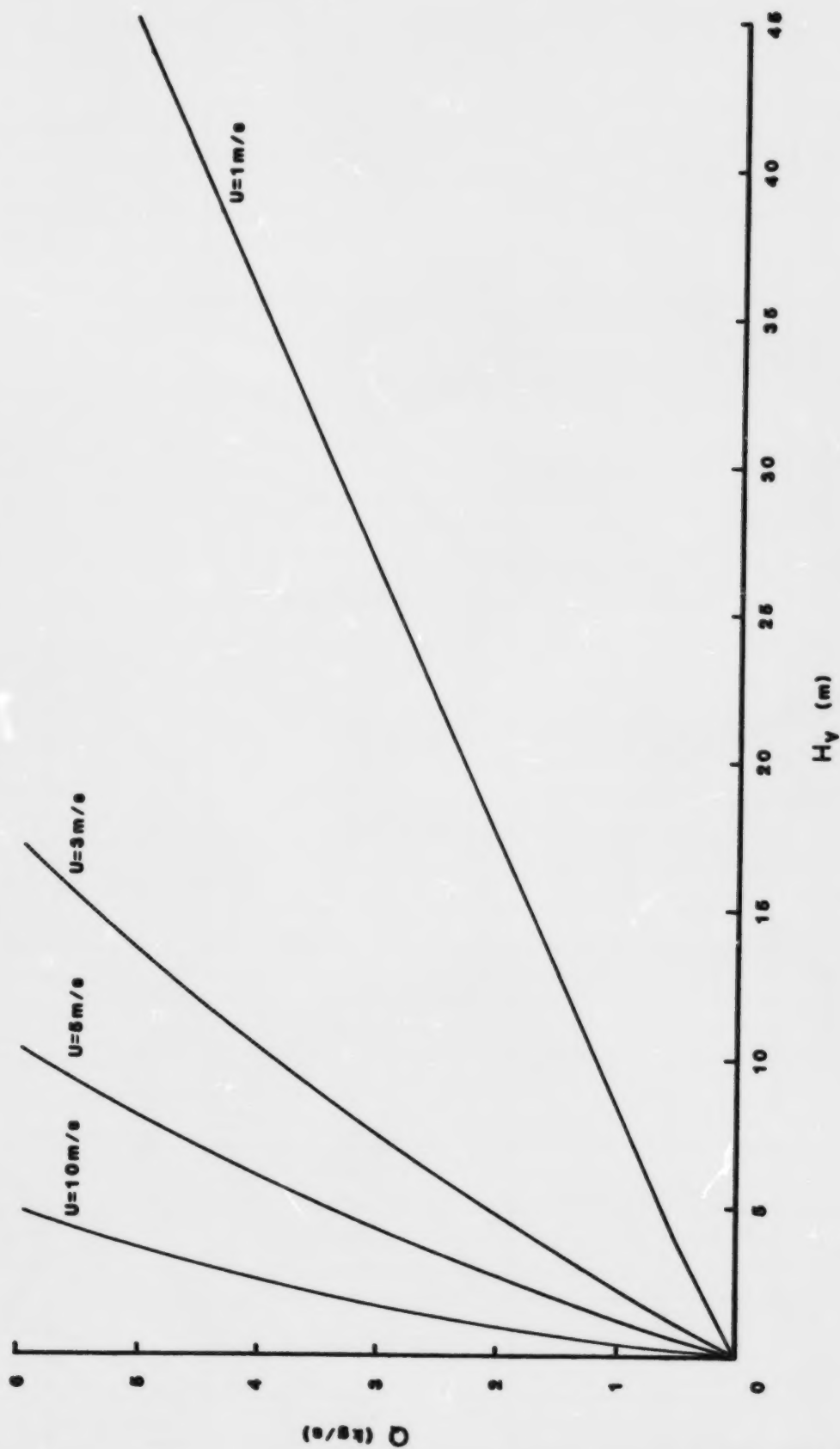
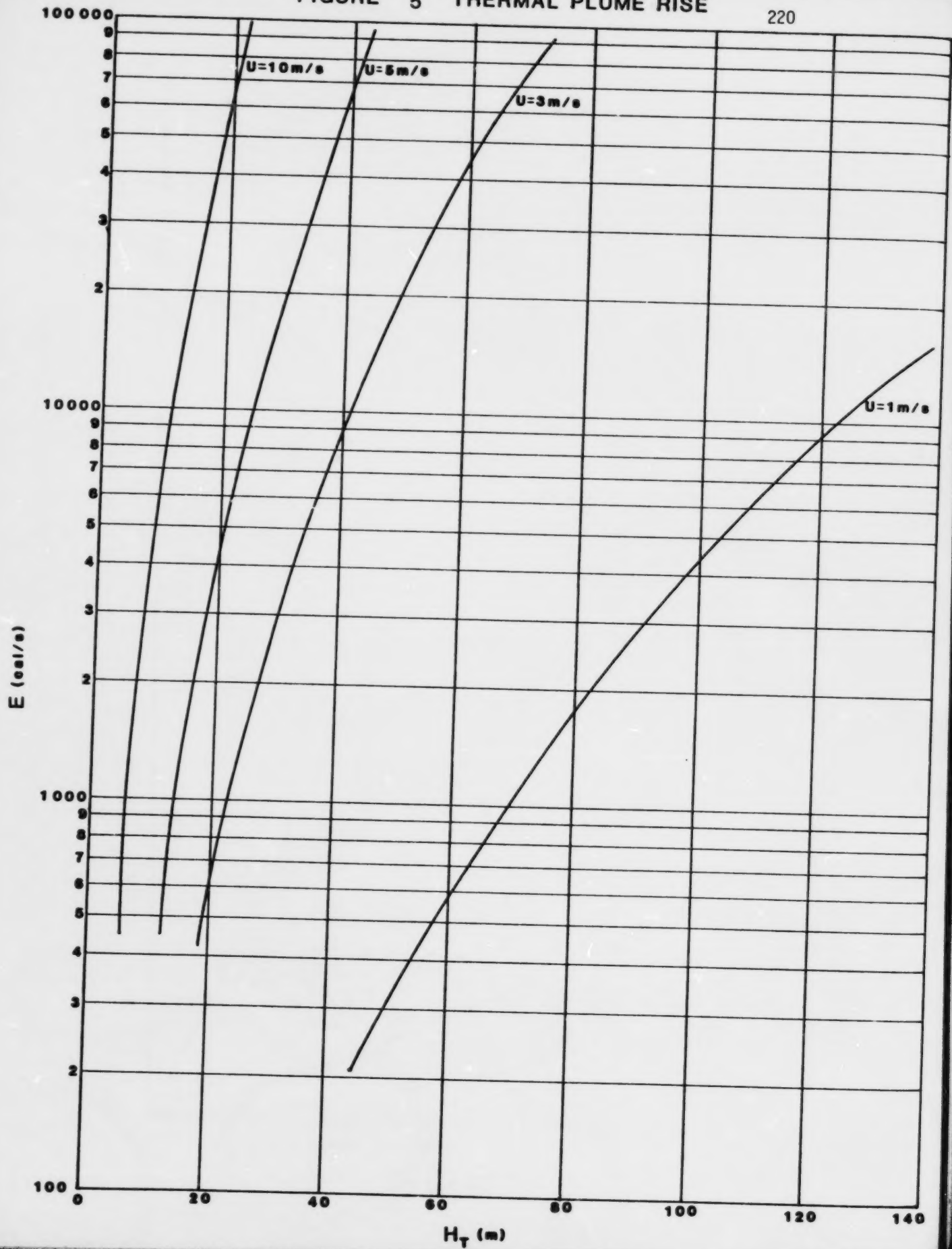
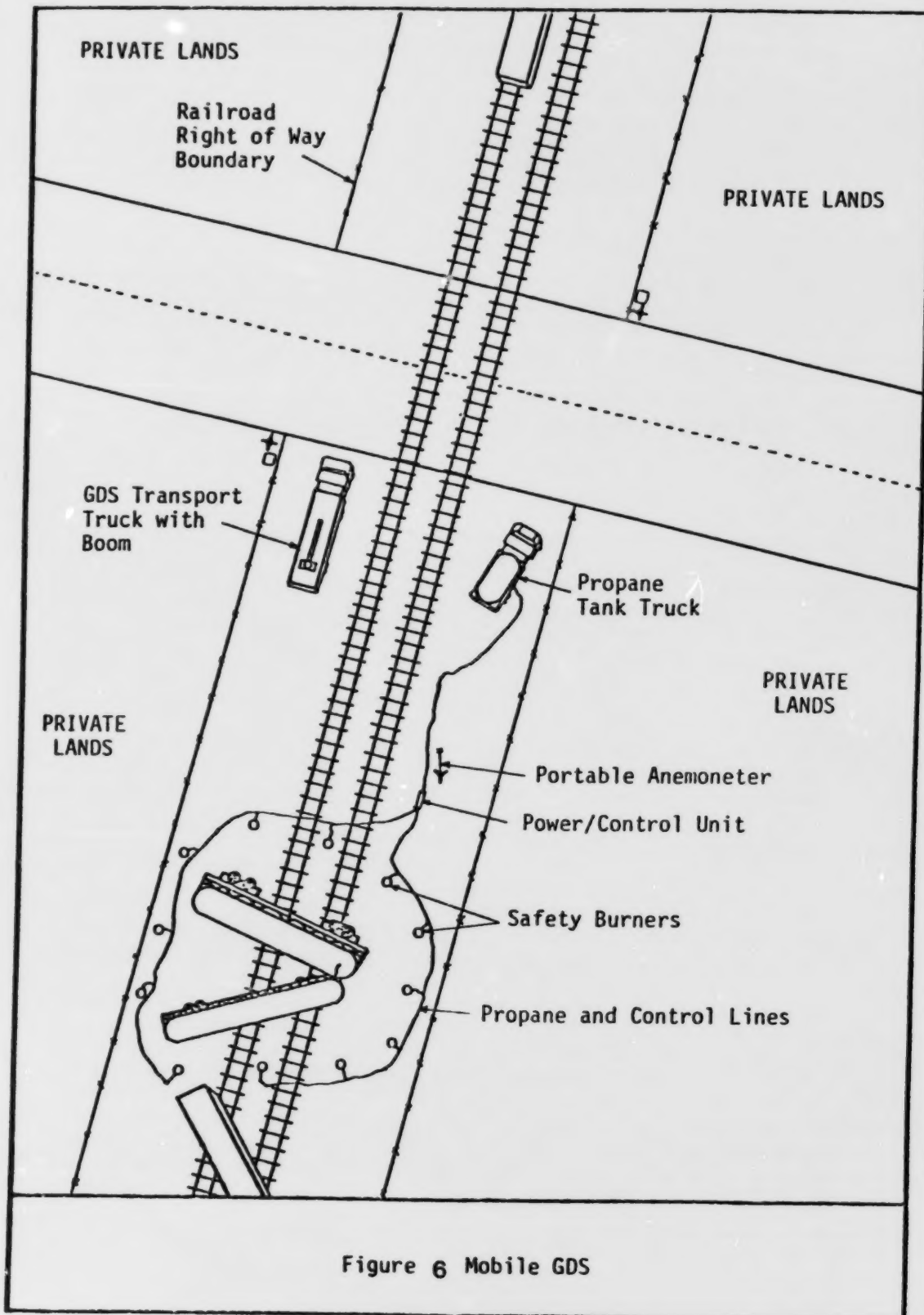


FIGURE 5 THERMAL PLUME RISE

220





The rate of fuel flow to a burner must balance flashback (when flame travels back into a premix burner) against flame blow-off (when the exit velocity of the fuel/air mixture exceeds the flame velocity). For premix burners (the most likely configuration for vapour spill control since the provision of pure vapour cannot be guaranteed), this is usually accomplished by using a narrow diameter fuel/air feed line (for high flow velocities) followed by an expansion/combustion section to reduce flow velocities to below the critical flame velocity. Safety factors of a least 5 are used for published flame velocity data. Table 3 shows published combustion data for most of the vapours and gases of concern.

Flare stacks are commonly used in the petroleum industry for combustion of waste gases and as emergency gas disposal systems. The general design rule for flare sizing is that the exit velocity of the gas should be 20 percent of sonic for regular operations and never exceed 30 percent of sonic for emergency flaring (Oenbring and Sifferman, 1980).

Figure 7 shows the required flare diameter (nozzle-mix) as a function of gas flowrate for three representative pure substances hydrogen, natural gas (methane) and benzene vapours. A 40 cm diameter flare would be able to deal with the combustible gases or vapours over a wide range of release rates.

Figure 8 shows the required burner diameter (pre-mix) as a function of gas release rate and concentration.

Obviously, much larger diameters are required for pre-mix burners than for the nozzle-mix flare. In addition, the vapour collection system and pre-mix burner must be designed to ensure that the concentration of gas collected is above the lower flammability limit and that the mixture velocity always exceeds five times the maximum flame velocity to prevent flashback. The use of this type of burner seems feasible but requires further research, probably involving actual testing.

Products of Combustion

Gaseous fuels are dispersed easily in air and combustion time is short once the ignition temperature is reached. The combustion process takes place in two ways depending on whether fuel and air are pre-mixed or not (Perry and Chilton, 1973).

In pre-mix burners the hydrocarbons and oxygen form hydroxylated compounds which become aldehydes. The addition of heat breaks down the aldehydes to H_2 , CO , CO_2 and H_2O . Since carbon is converted to aldehydes in the initial stages of mixing, no soot forms.

In nozzle-mix burners, soot and carbon black can form if insufficient oxygen is added to the fuel after heating and decomposition into carbon and hydrogen.

The major products of combustion for the priority chemicals are water, carbon dioxide and nitrous oxides. The combustion of carbon disulphide produces SO_2 , a component of acid rain and the combustion of chlorine compounds will produce ClO_2 a highly reactive (even explosive) compound. Mixtures of ClO_2 and air containing less than 6 kPa partial pressure of chlorine dioxide (about 6 percent by volume) are considered safe.

For each potential application of combustion as a vapour spill control countermeasure, a decision on the relative hazard of the compound versus its combustion products will have to be made.

FIGURE 7 NOZZLE-MIX FLARE SIZES

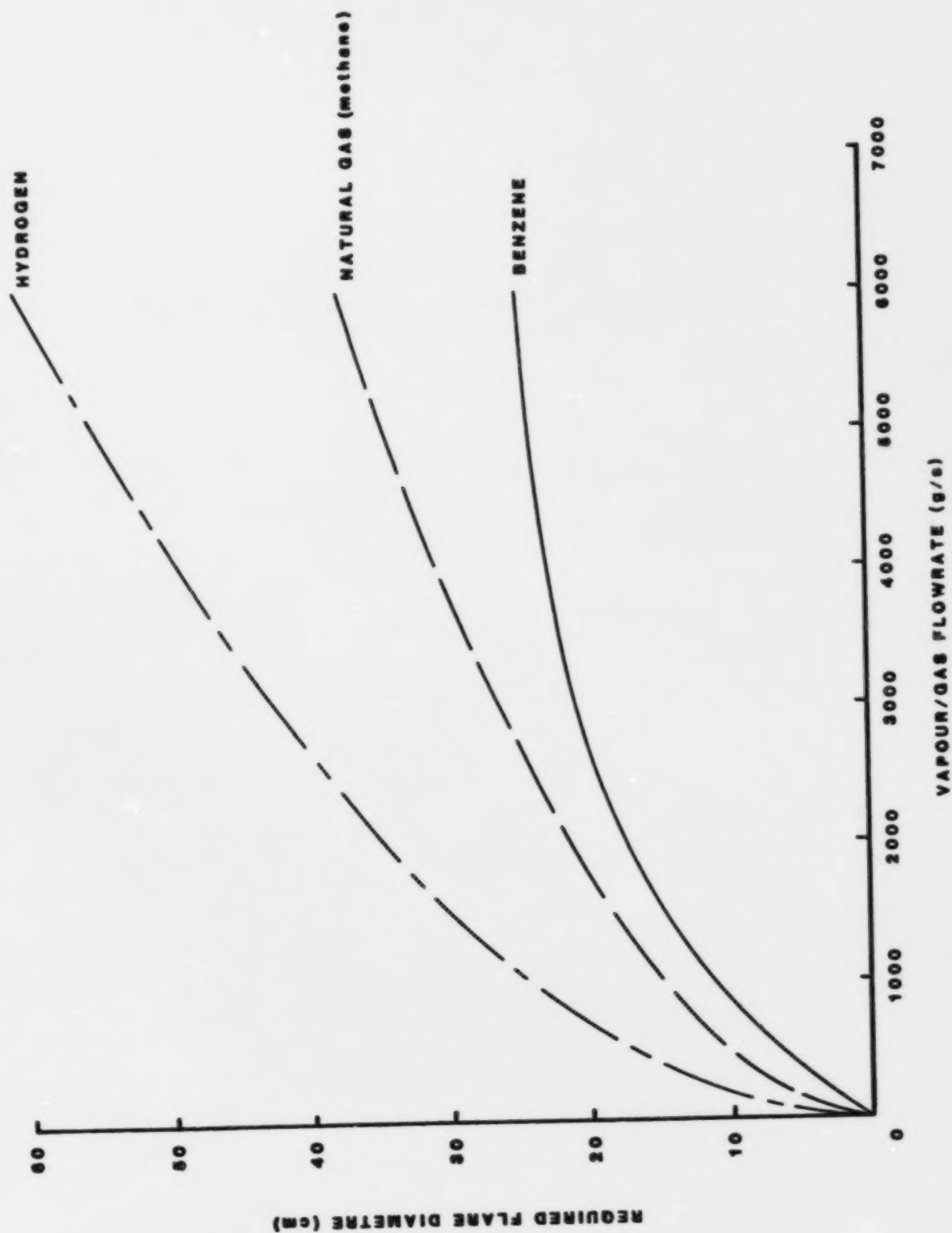
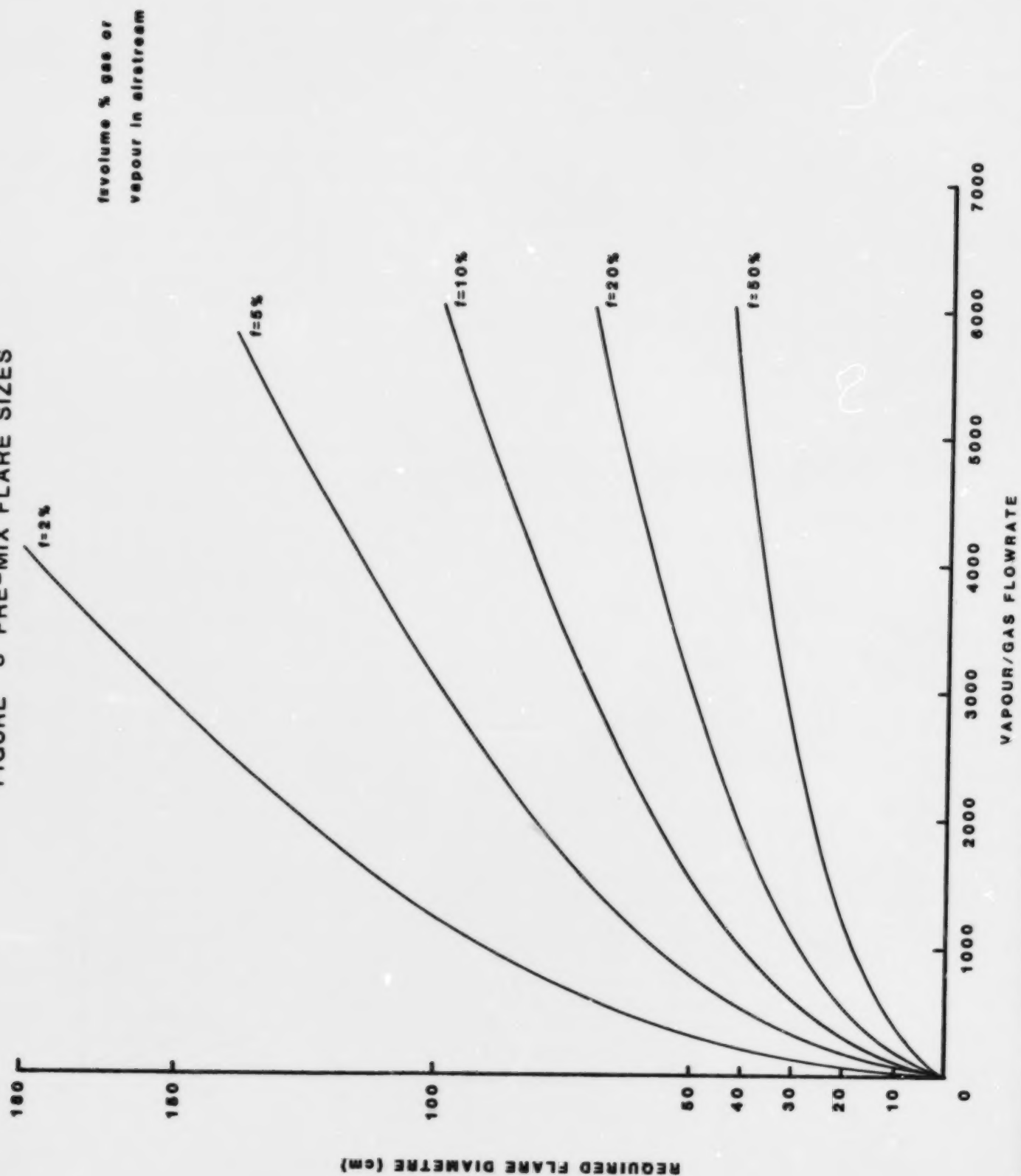


FIGURE 8 PRE-MIX FLARE SIZES



Heat is also a product of combustion. The fraction of a substance's heat of combustion that is radiated ranges from 0.25 for low molecular weight gas (methane) to 0.5 for higher molecular weight vapours (MW = 40) (Oenbring and Sifferman, 1980). Table 3 shows the permissible heat flux (including solar radiation) for personnel as a function of exposure time. These values and the gas properties were used to estimate flare stack heights.

Assuming 50 percent of combustion is radiated, a solar heat flux of $960 \text{ J/m}^2\text{s}$ (300 BTU/hr ft^2) and a heat of combustion of $4.6 \times 10^7 \text{ J/kg}$ ($20,000 \text{ BTU/lb}$) the height of the flare stack to permit safe working conditions for the entire area can be calculated. The results are shown in Table 3.

TABLE 3
FLARE STACK HEIGHT

<u>Vapour/Gas Burning Rate (kg/s)</u>	<u>Required Height of Stack (m)</u>
0.5	30
1	45
4	90
6	110

Since the erection of a stack higher than 40 m at the scene of an accident in a reasonable time is unlikely, a remote system would have to be designed to handle large flow vapour leaks. Research on the most applicable flare type (nozzle or premix), sizing, steam injection and ignition systems is recommended.

Compression/Condensation

Recompression of the vapour followed by condensation at ambient cooling water temperatures proved unfeasible for a portable system.

Refrigeration and Joule-Thompson systems for liquefaction at ambient pressure were rejected because of the potential icing problem with entrained, humid air.

Figure 9 shows the range of power requirements (isothermal to adiabatic) for compression of the priority chemicals (with boiling points below 20°C) to their vapour pressure at ambient temperature. Power requirement in excess of 100 kW preclude easy portability.

Figure 10 gives an example of the heat-transfer area and cooling water required for the condensation of a pressurized pure vapour at its boiling point. The presence of an inert gas (i.e. air) can increase the heat transfer areas by a factor of ten.

Absorption/Adsorption

Absorption in solvents was rejected because most of the priority chemicals are not appreciably soluble in water, the most easily available solvent and the required volumes of appropriate solvent (i.e. alcohol) prohibit portability. As an example, one 10 m^3 (22,000 gal) vacuum truck (a readily available piece of equipment that could be modified to scrub vapours) containing water could absorb, at best, about 5 percent of the material contained in a railway tank car.

FIGURE 8 PRE-MIX FLARE SIZES

180 °

FIGURE 9 VAPOUR COMPRESSION POWER CURVES

CONDITIONS
 $P = 101325 \text{ kPa}$ $\varphi = 1.5 \text{ kg/m}^3$ $k = 1.3$

LEGEND
 isothermal compression
 range of polytropic
 adiabatic compression

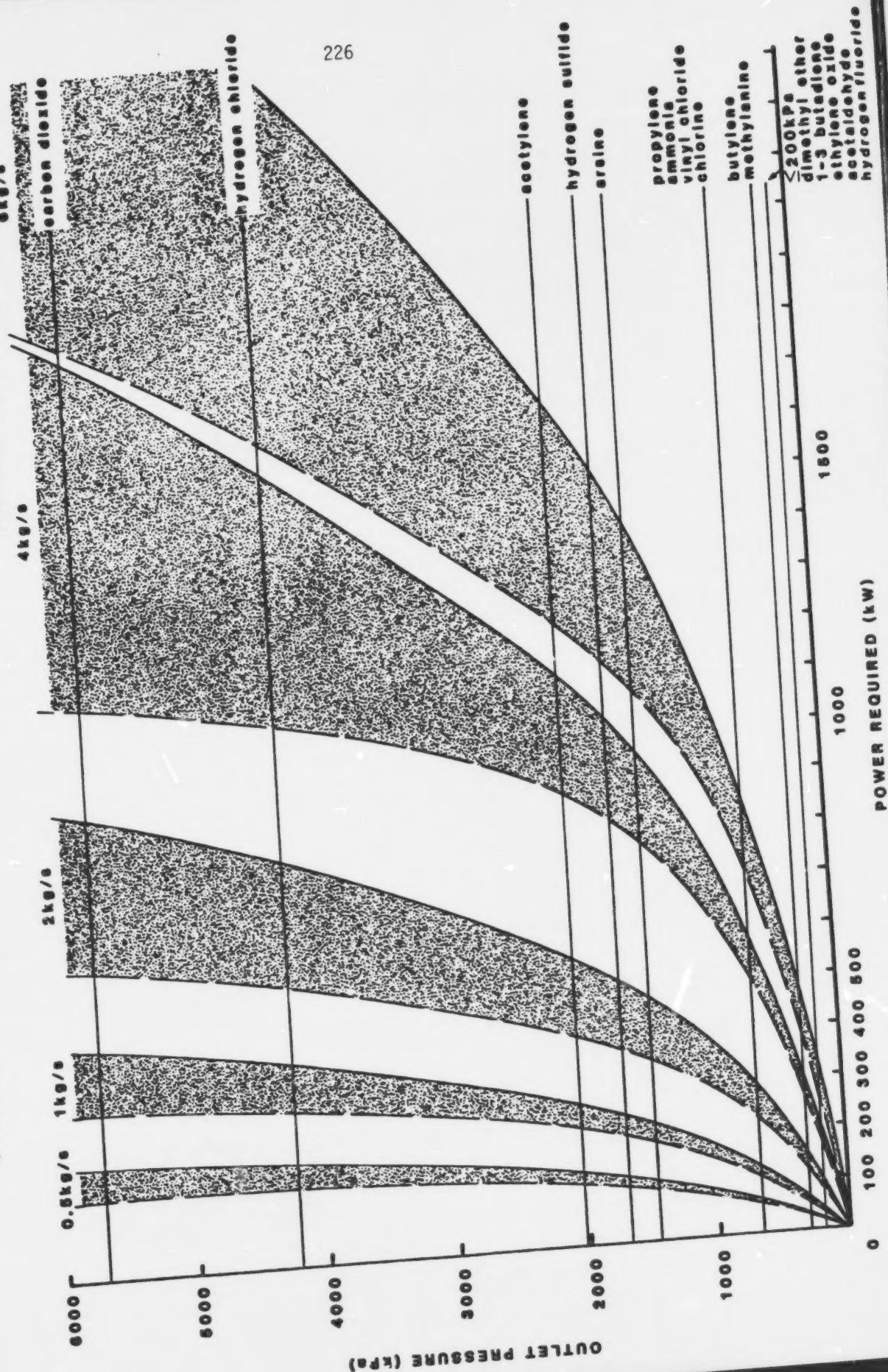
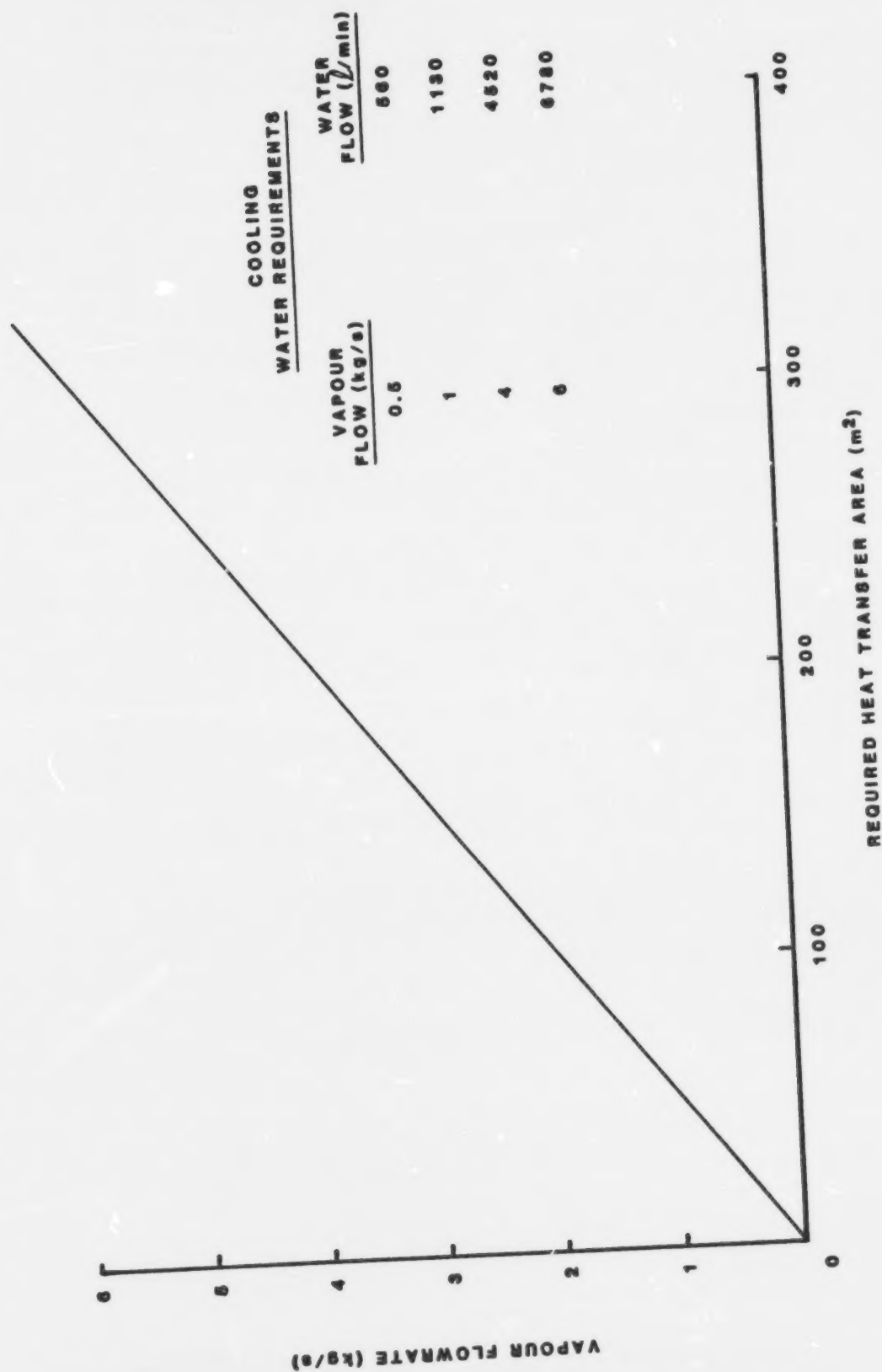


FIGURE 10 HEAT TRANSFER AREA REQUIRED FOR
CONDENSATION OF SATURATED VAPOUR IN HORIZONTAL
WATER-COOLED SHELL AND TUBE HEAT EXCHANGER



The use of activated carbon to adsorb vapours or gases is similarly constrained. The retentivity of the priority chemicals on activated carbon ranges from negligible to 45 percent by weight. Using the same vacuum truck example some 50 units would be required to deal with one railway tank car.

CONCLUSIONS AND RECOMMENDATIONS

Of all the concepts examined, lifting and dispersing the vapour or gas plume is by far the most feasible vapour spill control technique. Although the approach does not recover the contaminant or render it harmless the risk to human health and the immediate environment is greatly reduced. Further research and development on portable stack, fan and inert gas heater systems and/or the "Mobile Gas Dispersion" system is recommended.

The second most promising system for vapour spill control is the use of a burner or flare to combust the escaping substances. This system has a lesser applicability than dispersion (only 23 of the 33 priority chemicals are flammable), involves more risk and requires more development. Despite these potential drawbacks further R&D is recommended since combustion destroys the toxic substance at or near source, thus eliminating any downstream hazards. The issue of combustion products must also be addressed.

The use of absorption, adsorption recompression and condensation/liquefaction does not appear feasible for vapour spill control purposes because of the weight of materials and equipment required vis a vis a quick spill response.

CLEANUP OF PCB CONTAMINATED GROUNDWATER
BY REVERSE OSMOSIS

H. Whittaker
R. Clark

EETD
Neyrfor Turbodrilling of Canada Ltd.

Introduction

A 1976 rupture of an underground pipeline resulted in contamination of the soil at a western Canadian location with Interteen 70-30 solution which contains PCB's. Remedial measures have contained the spill but PCB contaminated groundwater is collected on site. In October 1984, Environment Canada's Mobile Reverse Osmosis (RO) Unit was shipped west. A trial was carried out to determine if RO could be used to reduce the amount of contaminated water. An objective of 6.5 ppb in the permeate was set.

Background

In 1976 an underground pipeline carrying Inverteen 70-30, which contains 70 percent PCB's and 30 percent tri and tetra-chlorobenzenes (TCB's) ruptured at the plant. The amount lost is not exactly known but exceeded 6,500 litres.

Remedial measures undertaken included collection and storage of highly contaminated soil, installation of a slurry wall and cap and installation of a sump system (Figure 1). The combination of the slurry wall, cap and sump system appears to have altered the underground flow and contained the PCB contaminated groundwater (Figure 2). There are, however, at least 43,000 litres of contaminated groundwater collected annually by the sump system. This water is stored in a tank but currently must be shipped to Oregon where a PCB licensed landfill exists. Shipment to that site costs 66¢ per litre (\$3.00/Imperial gallon).

In March 1984, during demonstration of the Mobile RO unit as a spilled wood preservative cleanup equipment, EPS personnel were approached concerning the possibility of using that process as a remedial measure. The mobile RO unit left Ottawa in early October for a trial on the PCB contaminated leachate. A consultant had agreed to pay all costs involved with the trial. The objective was to process 43,000 litres of contaminated water accumulated during the year and stored in a 50,000 litre tank.

Treatment of Contaminated Groundwater

The mobile RO unit was configured with two banks of 6 membrane elements each, one bank of Torays and one bank of DSI's. The trial commenced on 15 October. Start-up was delayed by a loose screw on the RO unit feed pump. Once that problem was corrected, the unit was set up for operation as shown in Figure 3. The unit was operated for 50 minutes at low pressure to condition the membranes on the feed with the produced permeate and concentrate being recycled to the feed tank. After that time, the pressure was increased to 5,500 kPa (800 psi) and the permeate and concentrate fed to storage tanks. Operation continued for 97 minutes then the unit was shut down for the night and kept heated.

The weather was much worse the next morning, however the hoses which had not been drained or heated did not appear to be frozen. The unit was, accordingly, started up. Within two minutes, the concentrate gauge split and the unit was shut down. A thorough check of the system revealed that chunks of ice had blocked the valve and overpressured the gauge. Repairs, which included a new concentrate gauge were required. The weather had shut down the airport so no parts could arrive and the trial was suspended for 30 hours. Once the gauge arrived, on 17 October, it was installed and a leak test was run on the RO unit. No leaks were discovered and recommencement of the trial was scheduled for 0800 on 18 October.

The plumbing was reconnected and the RO unit operating by 0900 on 18 October. The unit was run until 1730 at which time a leak in the diesel engine oil filter necessitated shut down. During the eight hours of operation the concentrate flow rate dropped steadily. Washing with feed gave only temporary relief. Details of the operation are included in the results section of this paper. Upon shut down the RO unit was flushed with acidified permeate (pH_3) then heated as previously but the hosing was disconnected and placed indoors. This procedure was successful in preventing further problems.

The same operating procedures were followed on October 19th and 20th for a total of 17 1/3 hours of operation at permeate flow rates from 15 to 37 litres per minute at concentration ratios of 5:1 to 8:1. The air temperature was -1°C during the day and lower at night during these two days. The feed temperature was approximately 6°C to 7°C .

On October 21, the remaining aqueous feed was exhausted, the fluid near the bottom of the 50,000 litre tank contained oils, sludge and debris. As the bottom was approached, the fluid was transferred into open top drums, where the floating sludge and ice could be skimmed off. While time consuming, this process allowed some protection of the RO unit. During operation, the air temperature hovered near -5°C .

A second pass using the 7,700 litres of concentrate as feed was commenced on 22 October and continued for two days. Flow rates were much lower during this period and concentration ratios above 3:1 were impossible to maintain for any period of time. Late in the day on 23 October a slight yellow tint was noticed in one of the permeates indicating a possible membrane problem. The unit was accordingly shut down and the trial terminated. At this time the concentrate had been reduced to 2,700 litres.

Cleansing of the unit was carried out by first flushing with acidified (pH_2) permeate. This was designed to remove any inorganic scaling from the membranes. It was followed by a flush with 200 litres of 10 percent methanol in permeate to remove any residual PCB's from the membranes and then flushed with permeate. The unit was then prepared for shipment back to Ottawa.

Results

When EETD was originally requested to provide assistance in a trial on reverse osmosis on the contaminated water, it was advised that the PCB concentration was approximately 30 ppb. A sample was subsequently requested and was provided. Analysis by River Road Environmental Technology Centre revealed that the PCB concentration in the sample was in fact 15 ppb but that the water contained high levels of inorganic salts and organic species. Results of the inorganic analysis are contained in Table 1.

TABLE 1

INORGANIC ANALYSIS OF CONTAMINATED GROUNDWATER

<u>CATIONS (PPM)</u>		<u>ANIONS (PPM)</u>	
SODIUM	256	FLUORIDE	326
CALCIUM	218	CHLORIDE	360
MAGNESIUM	67	SULPHATE	392
IRON	0.3	CARBONATE	321
MANGANESE	3		
POTASSIUM	18		

It was therefore decided that the groundwater would be acidified to pH 4.5 to 5.5 to prevent scaling on the membranes. This was done by adding approximately 33 kg of 30 percent HCl to the feed tank and recirculating. Because insufficient time and mixing energy were available to ensure complete mixing, the feed pH at start-up was between 6.0 and 7.0.

Physically, the feed solution was a slightly viscous very light yellow-grey liquid with a slight odour of organics. Upon processing by reverse osmosis (first pass) a clear, colourless permeate and a medium yellow concentrate the latter with a very pungent odour resulted. The presence of organics and oil in the feed was especially evident in the concentrate. This solution contained small droplets of an immiscible oily liquid which coalesced into a thin layer on top of the aqueous phase.

The second pass on the concentrate resulted once more in a clear, colourless permeate. The concentrate produced was, however, a deeper yellow than the feed and was noticeably more viscous. PCB analysis of permeate samples taken during the first and second passes was carried out by EnviroTest Laboratories of Edmonton under contract to EPS. Results are as shown in Table 2.

TABLE 2

PCB ANALYSIS OF COMBINED PERMEATE SAMPLES

<u>SAMPLE</u>	<u>RESULT</u>
84 10 18 PERMEATE FIRST PASS	0.03 μ g/l Arclor 1254
84 10 19 PERMEATE FIRST PASS	0.20 μ g/l Arclor 1254
84 10 20 PERMEATE FIRST PASS	0.18 μ g/l Arclor 1254
84 10 22 PERMEATE 2ND PASS	0.27 μ g/l Arclor 1254

It is possible to sample from four of the pressure vessels and this was done. Samples were transported back to RRETC for later analysis. This was done so that comparison of the DSI 441 and TORAY SP110 membranes could be carried out. Results of the analysis, carried out by Mann Testing Laboratories, under contract to EPS, are shown in Table 3.

TABLE 3

PCB AND TOC ANALYSIS OF FEED, CONCENTRATE AND INDIVIDUAL PERMEATES

<u>SAMPLE</u>			<u>RESULT</u>	
			<u>PCB (PPB)</u>	<u>TOC (PPM)</u>
FEED	-	FIRST PASS	24.0	87.0
P ₁ (DSI)	-	FIRST PASS	TRACE	9.0
P ₂ (DSI)	-	FIRST PASS	0.07	16.0
P ₃ (TORAY)	-	FIRST PASS	NID	28.0
P ₄ (TORAY)	-	FIRST PASS	NID	75.0
CONCENTRATE	-	FIRST PASS	4.1	480.0
P ₁ (DSI)	-	2ND PASS	TRACE	72.5
P ₂ (DSI)	-	2ND PASS	0.16	130.0
P ₃ (TORAY)	-	2ND PASS	NID	210.0
P ₄ (TORAY)	-	2ND PASS	NID	31.0
CONCENTRATE	-	2ND PASS	6.8	680.0

NOTE: CONCENTRATE - FIRST PASS was the FEED - 2ND PASS
TOC IS TOTAL ORGANIC CARBON

Although the rejection achieved by the RO membranes is important, the flux (flow-rate of the permeate) and the durability are of equal importance. A membrane which has a very high rejection but which fouls easily or has a very low flux is of limited use. During this trial, the combined permeate flow was measured at least once per hour and the individual flows were measured once during the first pass and once during the second. From this data, as shown in Table 4 and Figure 4, it is possible to determine the short term fouling rates and the permeation rates achievable using these membranes under the test conditions.

TABLE 4

PERMEATION RATES FOR INDIVIDUAL MEMBRANES

	<u>FIRST PASS</u>	<u>2ND PASS</u>
P ₁ (DSI)	3.5 l/min	2.3 l/min
P ₂ (DSI)	4.3 l/min	2.7 l/min
P ₃ (TORAY)	1.3 l/min	1.0 l/min
P ₄ (TORAY)	3.5 l/min	1.5 l/min

As previously noted, a slight yellow tint was noticed in the combined permeate shortly before the termination of the trial. This was later traced to a DSI 441 membrane element which had begun to fail. That particular membrane element had been used previously for:

- a. 70 hours on wood preservative; and,
- b. 710 hours on dilute chemical leachate.

The Toray membranes and the other DSI's had not been used on wood preservative. Failure may thus not be indicative of an inferior membrane element.

Discussion

The purpose of this trial was to determine if reverse osmosis could be used to reduce the volumes of PCB contaminated groundwater which would require further treatment or shipment to a secure landfill. The discharge level for the permeate had previously been set at 6.5 ppb by provincial authorities. During the trial, 43,000 litres of contaminated feed was treated to give 3,000 litres of concentrate and 40,000 litres of permeate, the latter having a PCB concentration of less than 0.270 ppb. As such, the trial is considered to have been successful.

Shipment of the 43,000 litres of contaminated groundwater to the designated landfill would have cost \$28,500. For the 3,500 litres of concentrate, this cost will be \$3,500. All costs for the trial, including shipping, fuel, operator costs, expendables and parts comes to \$12,500. A financial saving was thus achieved.

In this instance, it was not necessary to purchase an RO unit. A small unit capable of treating 43,000 litres of groundwater in a month or less would cost approximately \$35,000 including membranes. This unit could be operated by on-site personnel and increased cost should, therefore, be marginal. The unit would be paid for in decreased transportation costs, within two to three years.

It had been intended to decrease the pH of the feed solution from 7.7 to 4.5 - 5.5 by addition of HCl. The pH was, in fact, close to 6.5 for most of the trial. The decrease in flux which occurred each day was probably the result of short term scaling from calcium carbonate and sulphate salts present at that pH. After the trial, the membranes were cleaned and the flux restored to initial values.

Two different membranes were used, Toray SP 110's and DSI 441's. It is apparent from the analysis results that the Toray gave better PCB rejections. It is noted, however, that the permeate from both types exceeded the Saskatchewan Environment requirement by a factor of 20 or more. It should thus be possible to use a membrane with lower exclusion levels and higher flux rates while still meeting or exceeding the requirement.

The apparent discrepancy between the levels of PCB's in the combined and individual permeates indicates that the leaking membrane element was in a pressure vessel which does not have a sample port. A comparison of the raw feed with the two concentrates indicates that the majority of the PCB's were attached to suspended solids which were removed by the 25 μ filters in the unit or were in the oils which separated from the aqueous solution.

Although adverse weather conditions interfered with the trial, they did not prevent successful completion.

Conclusion

It is concluded that reverse osmosis is capable of reducing the amount of PCB contaminated groundwater from a situation such as this.

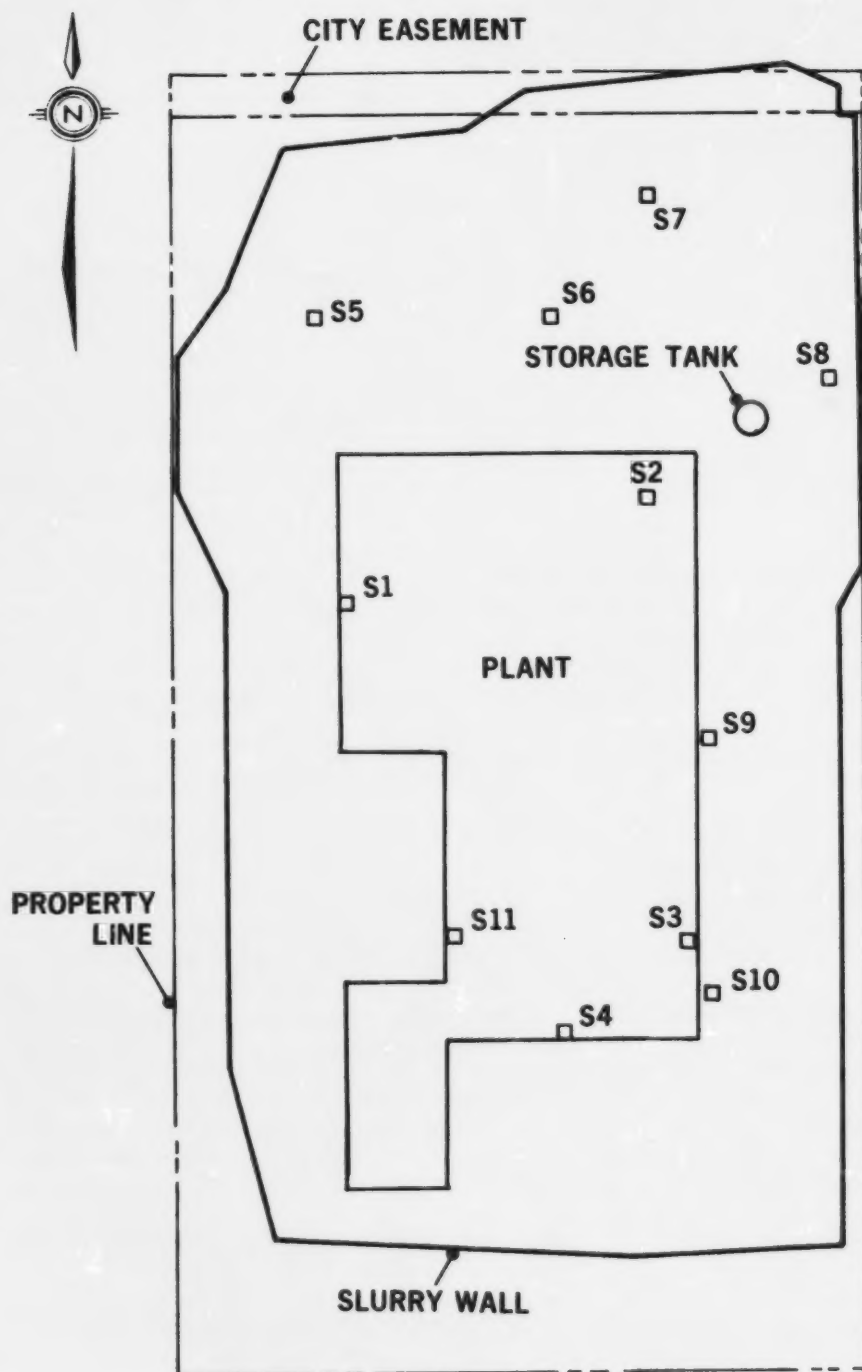


Figure 1. CONTAINMENT AND SUMP SYSTEM

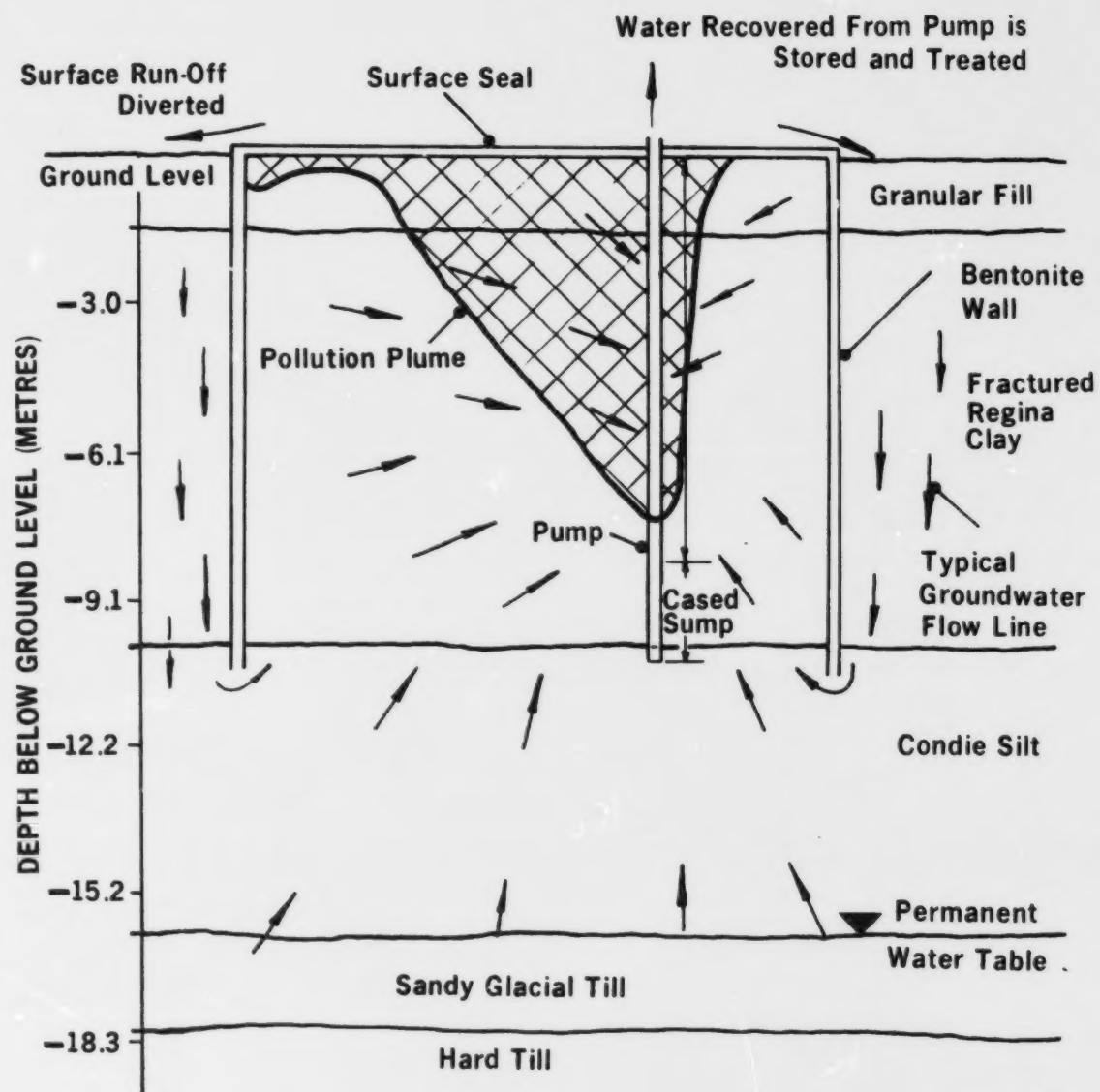


Figure 2. SECTION OF GROUND UNDER PLANT SHOWING CONTAMINATED GROUNDWATER

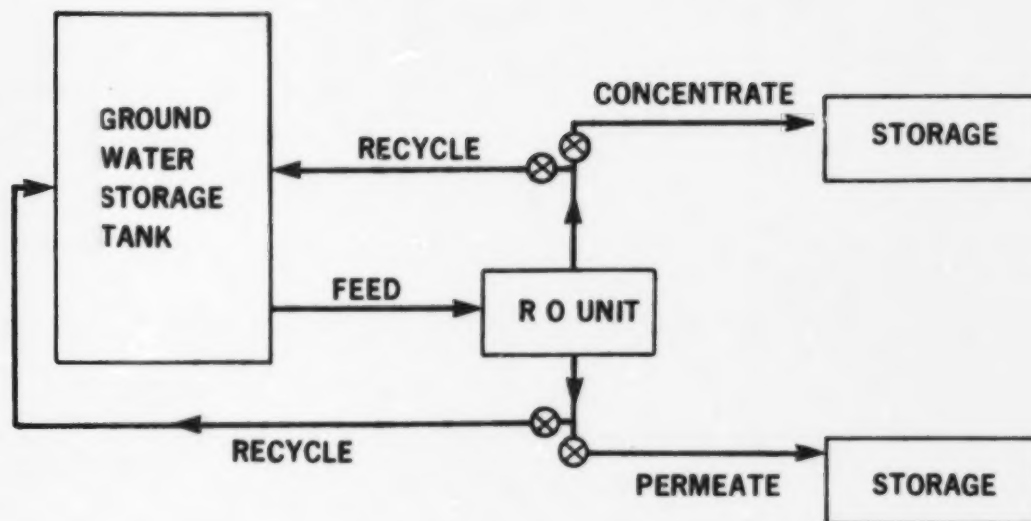


Figure 3. SET-UP FOR GROUNDWATER PROCESSING BY REVERSE OSMOSIS

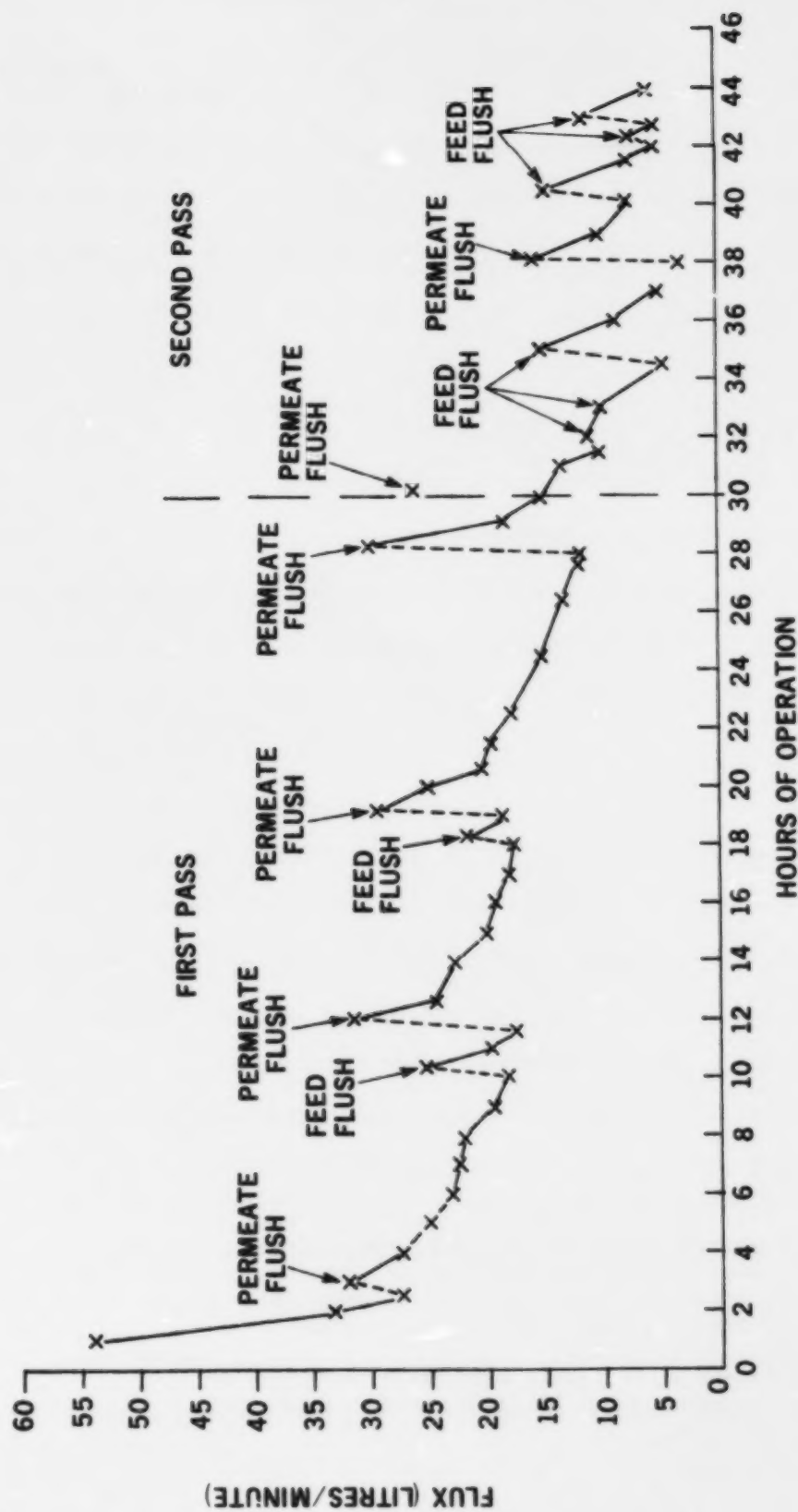


Figure 4. VARIATION OF PERMEATE FLUX WITH TIME FIRST PASS

DEVELOPMENT OF A GUIDANCE MANUAL FOR THE SELECTION AND USE OF SORBENTS
FOR LIQUID HAZARDOUS SUBSTANCE RELEASES

by R. Melvold¹, S. Gibson¹, R. Scarberry², W. Ellis ², and M. Royer³

ABSTRACT

This study was conducted to provide information for the selection and use of sorbents for cleanup or control of liquid hazardous substances. Literature reviews, sorbent manufacturer data and experiences of on-scene coordinators were reviewed in conjunction with laboratory studies. These laboratory studies determined the compatibility and sorption capacity of selected representative hazardous liquid-sorbent pairs. The combined experimental and literature data are being used to prepare A Guidance Manual for the Selection and Use of Sorbents for Hazardous Substance Releases. On-Scene Coordinators and their technical support personnel are the primary target audience for the manual.

To utilize the Manual, the user must first identify the spilled liquid. If it is one of the 200+ liquid hazardous substances addressed in the Manual, a reference is provided to one of 25 "Sorbent Selection and Use Guides". Each of the "Guides" enables the user to rapidly identify generic sorbent classes, physical forms, and methods for application and collection that are most suitable for each of four different chemical release-control scenarios: 1) a spill onto land; 2) a floating release into water; 3) a non-floating release into water; and 4) immobilization for landfilling.

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer review and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

¹ R. Melvold and S. Gibson are with Environmental Monitoring and Services, Inc., Newbury Park, CA.

² R. Scarberry and W. Ellis are with JRB Associates, McLean, VA.

³ M. Royer is with the U.S. Environmental Protection Agency, Edison, NJ.

The Manual contains "Sorbent Data Sheets" for 13 generic classes of sorbents other than activated carbon. These data sheets contain information on manufacturers, acquisition costs, bulk density and sorbent limitations. The sorption capacity of 190 sorbent-chemical pairs was determined and recorded in the Manual. The Manual also includes cost and estimation procedures, test methods, hazardous liquid physical properties, and a description of the rationale for the release-control scenarios.

INTRODUCTION

Spills and releases of liquid hazardous substances pose a severe threat to the public and the environment. These substances may be released at fixed sites or during transportation accidents and generally require control and cleanup. Sorbents are potentially effective materials for cleaning up and controlling many releases of liquid hazardous substances. The Manual described in this article is designed to facilitate the selection and use of appropriate sorbents for treating releases of hazardous liquids. The Manual is targeted primarily to assist Federal On-Scene Coordinators (OSC's) and their technical support staffs, but is also applicable to emergency response, spill cleanup and industrial personnel who respond to releases of hazardous liquids and immobilize such substances prior to disposal.

Development of the Manual involved a review of the literature, sorbent manufacturers' data, OSC experiences, and laboratory studies. The laboratory studies determined the compatibility and sorption capacity of selected hazardous liquid-sorbent pairs. To establish a framework for the Manual, four liquid release-control scenarios were studied: 1) a spill onto land;

2) a floating release onto water; 3) a non-floating release into water; and 4) immobilization for landfilling. "Sorbent Selection and Use Guides" were developed which list sorbents for each release-control scenario. Sorbent Data Sheets were also prepared for each of 13 classes of sorbents. The Manual also provides information on sorbent application, collection and disposal, cost estimation procedures, test methods, hazardous liquid physical properties, and a narrative to enable selection of appropriate sorbents. The Manual is designed to provide information for rapid decision making and for conducting thorough evaluations of alternative sorbent-use strategies.

PROCEDURES

The Manual development project was completed in three phases. The approach and results of each phase are described below.

Phase 1: Information Collection and Test Plan Development

Development of a List of Applicable Hazardous Liquids

A list of hazardous liquids for which the Manual would be applicable was developed from the substances regulated by the Comprehensive Environmental Response, Compensation and Liability Act of 1980, PL96-150 (CERCLA). The CERCLA hazardous liquids of concern are 213 neat hazardous substances that meet the liquid criteria designation (i.e., that a substance possess a melting point at or below 77°F (25°C) and a boiling point at or above 50°F (10°C)). Waste mixtures were not considered.

These CERCLA-regulated liquid hazardous substances were placed into 27 classes according to functional groups (Herrick et al, 1982). Since it was

not possible to experimentally evaluate all of the CERCLA hazardous liquids, representative hazardous liquids were selected from each chemical class based on aqueous solubility, specific gravity, liquid surface tension, and viscosity. Table 1 lists the chemical classes and guide numbers to which each hazardous liquid was assigned.

Table 1. CERCLA Liquid Chemical Classes

Chemical Class	Guide #	Chemical Class	Guide #
Acidic compounds, inorganic	1	Esters and ethers	15
Acidic compounds, organic	2	Ethers, halogenated	16
Alcohols and glycols	3	Halides, inorganic	17
Aldehydes	4	Heavy metals	18
Aliphatic hydrocarbons	5	Hydrazines and hydrazides	19
Aliphatics, halogenated	6	Ketones	20
Amides, anilides, and imides	7	Nitro/nitroso compounds	21
Amines, alkyl	8	Organophosphates	22
Amines, aryl	9	Oxides, alkylene	23
Aromatic hydrocarbons	10	Peroxides	24
Aromatics, halogenated	11	Phenols and cresols	25
Basic compounds	12	Sulfates and sulfites	26
Cyanates and isocyanates	13	Sulfides and mercaptans	27
Cyanides and nitriles	14		

Collection of Information

To complete the "Sorbent Selection and Use Guides" and the "Sorbent Data Sheets," pertinent data were collected. The physical data gathered for each liquid included specific gravity, aqueous solubility, surface tension, and viscosity. For physical data that was unavailable from technical reference materials and journals, the data were solicited from chemical manufacturers of the liquids.

A literature review was also conducted to identify available sorbents and their manufacturers, and to obtain published data on sorbent properties and performance. Based on information deficiencies noted in the available literature,

data sheets were requested from sorbent producers. Limited sorbent property and procurement information, and sorbent-hazardous liquid pair data such as sorption capacity, retention capacity, sorbent compaction and expansion data, performance parameters and safety precautions were obtained.

Test Plan Formation

For each chemical class, a representative chemical was chosen. Similarly, a representative sorbent was chosen from each of the 13 generic sorbent classes. Those representative sorbent-hazardous liquid pairs for which no data were available became primary candidates for testing. The selection of a hazardous liquid for testing considered the probability that a substance from one of the 27 chemical classes would be released and the degree of hazard that it would present to public health or the environment. Probability of a release was based on the annual production volume, while the degree of hazard was based on the proposed reportable quantity (RQ) of the CERCLA liquid as promulgated by the Environmental Protection Agency in 48FR23552-23605 and subsequent revisions. The sorbents were assigned a priority for testing based on 1) sorbent availability and 2) sorbent applicability for ameliorating a spill similar to one or more of the four cleanup scenarios. The following list presents the 13 generic sorbent categories identified by the project:

Sorbent Clay	Polyethylene
Diatomite	Polypropylene
Wood Fiber	Cross-Linked Polymer
Treated Wood Fiber	Feathers
Expanded Mineral	Treated Clay/Treated Natural Organic
Foamed Glass	Treated Expanded Mineral/Treated Wood Fiber
Polyurethane	

The sorbent-hazardous liquid pairs chosen for testing were from the top priority groups, resulting in selection of a maximum of 250 pairs from 23 chemical classes and 10 generic sorbents.

PHASE 2: Compatibility and Sorption Capacity Testing

Laboratory experiments and estimation procedures were employed in Phase 2 to generate or estimate sorbent performance data that were not available from the literature. The Phase 2 work included:

Compatibility Testing

A Standard Operating Procedure (SOP) was prepared that describes the procedures employed in conducting the compatibility tests. When a gross incompatibility was observed or degradation of the sorbent occurred, the sorbent-hazardous liquid pair was excluded from sorption capacity testing. Also, when the sorbent was not wetted by the hazardous liquid, the sorbent-liquid pair did not qualify for sorption capacity testing. The sorption capacity measurements of 190 sorbent-liquid pairs were conducted in Phase 2 of the project. The 10 sorbents tested for sorption capacity with the representative hazardous liquids were also tested for their sorption capacity with water. The data obtained were used in determining hazardous liquid/water preference indices for the sorbents.

Sorption Capacity Testing

The sorbent testing protocol consists of three procedures for three different sorbent forms: (1) A decanting procedure for particulate sorbents, in which after a 2-hour exposure in a graduated cylinder, the hazardous liquid is poured out through a stainless steel screen leaving behind the loaded sorbent for measurement; (2) A volume measurement procedure for finely-divided particulate

sorbents, wherein the sorbent is allowed to settle and the volume of the sorbent layer (and the liquid contained therein) is determined; and (3) A pad/mat immersion procedure, in which a standard-sized sorbent specimen is immersed in and then removed from a hazardous liquid and weighed after dripping ceases.

Sorbent/Hazardous Liquid Data Estimation

Project funds did not permit experimental determination of all sorbent-hazardous liquid sorption capacity values of interest. Procedures were established for estimating sorption capacities for cases where the untested sorbent-chemical pair was sufficiently similar to pairs for which data were available. The estimation procedures are not rigorously defensible from a scientific standpoint, but it was concluded that On-Scene Coordinators and their technical support personnel would be forced to develop similar estimation procedures when faced with hazardous liquid releases for which sorption capacity data did not exist. Therefore, the estimates were made, included in the Manual, and clearly marked as estimates.

Phase 3: Manual Preparation

This phase of the project involved the following activities:

- ° Development of the "Sorbent Selection and Use Guides"
- ° Preparation of the "Sorbent Data Sheets"
- ° Production of ancillary data tables:
 - sorption capacity
 - hazardous liquid/water preference
 - physical properties
 - test methods
 - equipment/sorbent costs
- ° Preparation of the handbook text

Description of these elements follows in the Results and Discussion section.

RESULTS AND DISCUSSION

A draft document, A Guidance Manual for the Selection and Use of Sorbents for Liquid Hazardous Substance Releases has been prepared, which contains eight sections. The first three sections, "Sorbent Selection and Use", "Sorbent Data", and "Technical/Logistical Information", are essential to users who require a condensed source of sorbent selection and use guidance. The other five sections, "Cost Estimation Procedures and Data", "Test Methods", "Spill Scenario Rationale", "Sources of Information", and "CERCLA Liquid Chemical Information," explain the rationale used to develop the condensed guidance in the first three sections and also provide information that enables the user to acquire and use sorbent information for specific needs. A synopsis of each of the eight sections is provided below.

Section A - "Sorbent Selection and Use"

Two CERCLA Liquids Indexing Tables are an integral part of Section A. The first indexing table lists CERCLA designated hazardous liquids, the chemical class and guide number to which each liquid has been assigned, the CAS number for each liquid, the hazards in addition to toxicity, and the behavior of the liquid in water. The second indexing table lists the 4-digit DOT ID number used in commercial shipping, and supplemental information similar to that in the first indexing table. Information is provided for all 213 CERCLA liquids that were identified.

Section A of the guide also contains the "Sorbent Selection and Use Guides". Each "Guide" presents information on the use of sorbents relevant to the four scenarios: Landspill, Floating Spill, Non-Floating Spill, and Landfill. Chemical functional classes are generally regarded to be descriptive of the

chemical reactivity of the CERCLA liquids; consequently, one guide was prepared for each chemical class for which data were available. Each guide lists generic sorbents, in recommended order for consideration for each of the four scenarios. An example of a "Sorbent Selection and Use Guide" is in Table 2. Application and collection procedures are listed in each "Guide" based on assessment of the optimal procedures for use with each generic sorbent. For each sorbent listed in each "Guide", the page number of the "Sorbent Data Sheet" is also included.

Section B - "Sorbent Data"

This section contains 1) an index of sorbent manufacturers, trade names, and generic sorbent categories, 2) 13 "Sorbent Data Sheets", 3) the sorption capacity data, and 4) the hazardous liquid/water preference indices.

A "Sorbent Data Sheet" was prepared for each generic class of sorbents. Each data sheet lists the generic sorbent class, commercial trade-names, manufacturers data on the types of sorbents, their cost, bulk density and storage requirements. The sorbent types generally available include: particulates, pillows, pads, mats, and booms. The data sheets also report limitations on the use of each generic sorbent for landspills, floating spills and non-floating spills. Hazards relative to gross incompatibilities, health, safety, and environmental concerns are delineated and the sorbent density is also given. The format allows for updating of the Sorbent Data Sheets as additional sorbents become available. An example of a Sorbent Data Sheet is shown in Table 3. Sorption capacity data for the representative sorbent-hazardous liquid pairs are also tabled in Section B (Table 4). Another table in Section B (Table 5) contains hazardous liquid-water preference indices, which are the the grams of hazardous liquid sorbed to the grams of water sorbed by the same quantity of

SORBENT SELECTION AND USE GUIDE

GUIDE NUMBER 10

CHEMICAL CLASS: Aromatic Hydrocarbons

REPRESENTATIVE HAZARDOUS LIQUID: Toluene

For releases onto land, recommended sorbents are listed in prioritized order under the Landspill Scenario, for water, under the Floating Spill or Non-Floating Spill Scenarios, and, for landfill applications, under Landfill Scenario. For additional sorbent prioritization information, see the Sorbent Prioritization tables on pages I-2 thru I-7, Section I of the handbook. Also, for additional sorbent specifics turn to the Sorbent Data Sheet found on the page listed in the prioritized sorbent column. Pertinent logistical information, such as application and collection methodology, is given in Section C of the handbook.

LANDSPILL - SMALL

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1) Feathers/pl/B-12	Throw	Pitchfork	DGC, RT
(2) CLP/p/B-11	Shovel	Shovel	R, W, SS
(2) CLP/pl/B-11	Throw	Pitchfork	R, DGC, RT
(3) Sorbent Clay/p/B-2	Shovel	Shovel	R, I, P
(3) TC/p/B-13	Shovel	Shovel	R, I
(4) Wood Fiber/pl/B-4	Throw	Pitchfork	R, P, DGC, RT

LANDSPILL - MEDIUM

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1) CLP/p/B-11	Blower	Skiploader	R/W/SS
(2) TC/p/B-13	Blower	Skiploader	R/I
(3) Sorbent Clay/p/B-2	Blower	Skiploader	R, I, P
(3) Polypropylene/p/B-10	Blower	Skiploader	W, SS, DGC
(3) Feathers/pl/B-12	Throw	Skiploader	DCG, RT
(4) Ex Mineral/p/B-6	Blower	Skiploader	R, I, W, P, DGC

FLOATING SPILL

NON-FLOWING - SMALL POND

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1) CLP/pl/B-11	Throw	Spear	R
(2) Feathers/pl/B-12	Throw	Spear	
(2) TW Fiber/pl/B-5	Throw	Spear	
(3) Polyurethane/m/B-8	Throw	Spear	
(4) Polypropylene/m/B-10	Throw	Spear	
(4) Polyethylene/m/B-9	Throw	Spear	

NON-FLOWING - LARGE LAKE

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1) CLP/pl/B-11	Boat/Throw	Boat/Spear	R
(2) Feathers/pl/B-12	Boat/Throw	Boat/Spear	
(3) TW Fiber/pl/B-5	Boat/Throw	Boat/Spear	
(4) Polypropylene/m/B-10	Boat/Throw	Boat/Spear	
(4) Polyurethane/m/B-8	Boat/Throw	Boat/Spear	
(5) Polyethylene/m/B-9	Boat/Throw	Boat/Spear	

FLOWING - SMALL CREEK

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1) Polypropylene/b/B-10	Hand	Hand	
(2) Polyurethane/b/B-8	Hand	Hand	
(3) Feathers/b/B-12	Hand	Hand	
(4) TW Fiber/b/B-5	Hand	Hand	
()			
()			

FLOWING - LARGE RIVER

Prioritized Sorbents/Type/Pg	Application	Collection	Limitations
(1) Polypropylene/b/B-10	Boat/Hand	Boat/Winch	
(2) Polyurethane/b/B-8	Boat/Hand	Boat/Winch	
(3) Feathers/b/B-12	Boat/Hand	Boat/Winch	
(4) TW Fiber/b/B-5	Boat/Hand	Boat/Winch	
()			
()			

NON-FLOWING SPILL

LANDFILL

COLUMN TREATMENT

BATCH TREATMENT

Prioritized Sorbents/Type/Pg	Limitations	Prioritized Sorbents/Type/Pg	Limitations	Prioritized Sorbents/Type/Pg	Estimated* Disposal Costs(\$)
(1) Polypropylene/p/B-10		(1) Feathers/pl/B-12		(1) Ex Mineral/p/B-6	1175
(2) TC/p/B-13	R, I	(1) Polyethylene/m/B-9		(2) TC/p/B-13	1358
()		(1) Polyurethane/m/B-8		(3) Sorbent Clay/p/B-2	1674
()		(1) CLP/pl/B-11	R	(4) Wood Fiber/p/B-4	2017
()		(2) Polypropylene/m/B-10		(5) Foamed Glass/p/B-7	3271
()		(3) CLP/p/B-11	R, RM	(6) Polypropylene/p/B-10	3852

* Cost includes sorbent, drums, mixing, transportation, and disposal associated with landfill of 1000 gals. of hazardous liquid.

Legend:

b	= Boom
CLP	= Cross linked polymer
DGC	= Not effective where ground cover is dense
Ex Mineral	= Expanded mineral
I	= Not incinerable
m	= Mat
p	= Particulate
P	= Effectiveness reduced when rainy

pl	= Pillow
R	= Not reusable
RM	= Removability (from batch contactor) is difficult
RT	= Not effective where terrain is rugged
SS	= Not for use within environmentally sensitive sites
TC	= Treated clay/treated natural organic
TW Fiber	= Treated wood fiber
W	= Effectiveness reduced when windy

TABLE 2 Sorbent Selection and Use Guide example

SORBENT DATA SHEET

GENERIC CLASS: Sorbent Clay

<u>SND-C, SMC-M</u> <u>Oil Dry Corporation</u> Chicago, IL 312-321-1515 o Cost: Particulate - \$0.05/lb o Bulk Density: 29-36 lb/ft ³ o Store: Dry	<u>Clean Dri, Quick Sorb, Absorbe-It</u> <u>Clean Up I</u> <u>Excel-Mineral Co.</u> Goleta, CA 805-683-5321 o Cost: Particulate - \$0.12/lb o Bulk Density: 34-38 lb/ft ³ o Store: Dry	<u>Safestep, Friction</u> <u>Andesite of California, Inc</u> o Cost: Particulate - \$0.49/lb o Bulk Density: 37 lb/ft ³ o Store: Dry
<u>Love's Safety Absorbent</u> <u>Love's, Inc.</u> South Ben, In 219-234-8191 o Cost: Particulate \$0.04/lb o Bulk Density: 42 lb/ft ³ o Store: Dry	<u>Waverly</u> <u>Waverly Mineral Products Co.</u> Bala Cynwyd, PA 215-668-2808 o Cost: particulate - \$1.50 o Bulk Density: 30-40 lb/ft ³ o Store: Dry	

NOTE: Sorbent Clays are commercially available as kitty litter

LIMITATIONS

Landspill
 Not reusable or incinerable, effectiveness reduced when rainy

Floating Spill - Non-Flowing Mode
 Not for use on spills into water

Floating Spill - Flowing Mode
 Not for use on spills into water

Non-Floating Spill
 Not for use on spills into water

PERFORMANCE

Sorption capacity data and hazardous liquid/water preference index information are given in Tables B1 and B2, respectively. If the sorbent/hazardous liquid pair is either observed or known to be incompatible, an "I" is given in the Table B1, or if the sorbent is not wetted by the hazardous liquid, an "NW" is used.

INCOMPATIBILITIES

- o Acidic compounds, inorganic
- o Halides, inorganic
- o Cyanates and isocyanates
- o Heavy metals

HEALTH/SAFETY CONSIDERATIONS

Wear dust respirator and eye protection when handling particulate and other protective equipment appropriate for the hazardous liquid.

ENVIRONMENTAL CONSIDERATIONS

Does not biodegrade, but is a natural component of the environment.

SORBENT DENSITY

137.2 pounds/cubic foot

TABLE 3. Sorbent Data Sheet example

TABLE 4 SORPTION CAPACITIES OF REPRESENTATIVE SORBENT/HAZARDOUS LIQUID PAIRS*

Chemical Class	Guide No.	Representative Hazardous Liquid	GENERIC SORBENT CLASS										
			SC	D	WF	TMF	EH	FC	PU	PE	PP	CLP	TC
Acidic compounds, inorganic	1	Nitric acid	I	I	I	I	7.1	[15.2]	I	I	NW	I	ND
Acidic compounds, organic	2	Acrylic acid	1.3	1.4	2.0	2.0	4.8	11.6	I	13.0	9.0	5.9	ND
Alcohols & glycols	3	Allyl alcohol	1.0	1.2	1.4	1.7	4.0	9.3	12.3	12.0	7.9	3.3	ND
Aldehydes	4	Furfural	1.2	1.7	2.3	1.7	5.4	11.5	18.1	12.8	11.0	4.3	ND
Aliphatic hydrocarbons	5	Isoprene	0.7	1.1	1.2	1.2	3.5	7.7	7.3	12.0	6.5	16.3	ND
Aliphatics, halogenated	6	Trichloroethylene	1.6	2.5	2.4	2.2	6.7	12.1	20.4	25.6	11.3	36.9	ND
Amides, anilides, & imides	7	Triethylamine	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Amines, alkyl	8	Pyridine	0.8	1.0	0.8	1.3	3.0	[8.6]	8.7	12.2	7.1	14.0	ND
Amines, aryl	9	Toluene	(1)	(2)	(2)	(2)	(5)	(11)	(18)	(21)	(11)	ND	ND
Aromatic hydrocarbons	10	Toluene	[0.8]	2.1	1.6	1.4	4.5	[9.2]	12.6	17.6	8.3	18.3	[6.1] [21.6]
Aromatics, halogenated	11	o-Dichlorobenzene	1.5	2.3	2.4	2.0	5.2	11.8	19.2	22.3	11.2	29.6	ND
Basic compounds	12	Ammonium hydroxide	1.0	I	I	I	4.1	13.3	NW	NW	NW	3.8	ND
Cyanates & isocyanates	13	Toluene diisocyanate	I	I	2.6	2.1	5.2	[14]	15.3	21.0	10.7	5.3	ND
Cyanides & nitriles	14	Acetonitrile	0.9	1.1	1.6	1.4	3.8	10.5	NW	10.0	8.6	2.7	ND
Esters & ethers	15	1,4-Dioxane	1.1	1.4	2.3	1.8	5.4	12.6	14.9	14.6	9.5	10.5	ND
Ethers, halogenated	16	2-Chloroethyl vinyl ether	(1.1)	(1.4)	(2.3)	(1.8)	(5.4)	(12.6)	(14.9)	(14.6)	(9.5)	(10.5)	ND
Halides, inorganic	17	Phosphorus trichloride	I	I	2.4	I	8.1	[14.4]	18.8	26.3	11.1	41.6	ND
Heavy metals	18	Lead fluoroborate	I	I	4.0	NW	I	I	NW	NW	NW	10.5	ND
Hydrazines & hydrazides	19	Methyl hydrazine	0.9	1.1	I	I	I	I	I	8.5	7.7	3.2	ND
Ketones	20	Methyl isobutyl ketone	1.0	1.2	1.4	1.3	3.8	6.7	9.0	10.7	6.5	12.7	ND
Nitro/nitroso compounds	21	Nitrobenzene	(1)	(1)	(2)	(2)	(5)	(12)	(14)	(13)	(10)	ND	ND
Organophosphates	22	Malathion	1.3	1.5	2.2	1.9	4.4	10.5	12.6	16.8	8.9	7.3	ND
Oxides, alkylene	23	Propylene oxide	0.8	1.1	1.4	1.1	3.8	8.9	12.4	12.2	7.9	11.4	ND
Peroxides	24	alpha, alpha-Dimethylbenzylhydroperoxide	1.1	1.5	2.6	1.7	4.8	12.5	25.1	15.8	9.3	3.9	ND
Phenols & cresols	25	Cresol	1.3	1.5	2.6	2.0	4.9	12.0	I	17.2	10.0	13.9	ND
Sulfates & sulfites	26	Dimethyl sulfate	1.3	2.0	2.1	2.3	5.9	13.1	15.5	14.6	11.2	5.2	ND
Sulfides & selenides	27	Carbon disulfide	1.3	2.0	2.7	1.9	5.5	[12.6]	14.4	13.1	11.9	30.2	ND
Water			1.0	1.4	3.3	1.0	5.5	12.9	2.4	1.4	0.1	2.5	ND

* The reported sorption capacity data are given in grams of hazardous liquid per gram of sorbent and were measured experimentally in the laboratory except as noted:
 () = estimated value
 [] = literature value

LEGEND:
 CLP = Cross-Linked Polymer
 D = Diatomite
 EH = Expanded Mineral
 F = Feathers
 FC = Foamed Glass
 I = Incompatible
 ND = No Data
 NW = Non-Wetting
 PE = Polyethylene
 PP = Polypropylene
 PU = Polyurethane
 SC = Sorbent Clay
 TC = Treated Clay/Treated Natural Organic
 TMF = Treated Wood Fiber
 WF = Wood Fiber

TABLE 5 REPRESENTATIVE HAZARDOUS LIQUID/WATER PREFERENCE INDICES*

Chemical Class	Guide No.	Representative Hazardous Liquid	GENERIC SORBENT CLASS									
			SC	D	WF	TWF	EM	FG	PU	PE	PP	CLP
Acidic compounds, inorganic	1	Nitric acid	**	**	**	**	1.3	[1.2]	**	**	**	**
Acidic compounds, organic	2	Acrylic acid	1.3	1.0	0.6	2.0	0.9	0.9	**	9.3	90.0	2.4
Alcohols & glycols	3	Allyl alcohol	1.0	0.9	0.4	1.7	0.7	0.7	5.1	8.6	79.0	1.3
Aldehydes	4	Furfural	1.2	1.2	0.7	1.7	1.0	0.9	7.5	9.1	110.0	1.7
Aliphatic hydrocarbons	5	Isoprene	0.7	0.8	0.4	1.2	0.6	0.6	3.0	8.6	65.0	6.5
Aliphatics, halogenated	6	Trichloroethylene	1.6	1.8	0.7	2.2	1.2	0.9	8.5	18.3	113.0	14.8
Amides, anilides, & imides	7	**	**	**	**	**	**	**	**	**	**	**
Amines, alkyl	8	Triethylamine	0.8	0.7	0.2	1.3	0.6	[0.7]	3.6	8.7	71.0	5.6
Amines, aryl	9	Pyridine	(1.0)	(1.4)	(0.6)	(2.0)	(0.9)	(0.9)	(7.5)	(15.0)	(110.0)	**
Aromatic hydrocarbons	10	Toluene	[0.8]	1.5	0.5	1.4	0.8	[0.7]	5.3	(12.6)	83.0	7.3
Aromatics, halogenated	11	o-Dichlorobenzene	1.5	1.6	0.7	2.0	1.0	0.9	8.0	15.9	112.0	11.8
-Basic compounds	12	Ammonium hydroxide	1.0	**	**	**	0.8	1.0	**	**	**	1.5
Cyanates & isocyanates	13	Toluene diisocyanate	**	**	0.8	2.1	1.0	[1.1]	6.4	15.0	107.0	2.1
Cyanides & nitriles	14	Acetonitrile	0.9	0.8	0.5	1.4	0.7	0.8	**	7.1	86.0	1.1
Esters & ethers	15	1,4-Dioxane	1.1	1.0	0.7	1.8	1.0	1.0	6.2	10.4	95.0	4.2
Ethers, halogenated	16	2-Chloroethyl vinyl ether	1.1	1.0	0.7	1.8	1.0	1.0	6.2	10.4	95.0	**
Halides, inorganic	17	Phosphorus trichloride	**	**	0.7	**	1.5	[1.1]	7.9	18.8	111.0	16.6
Heavy metals	18	Lead fluoborate	**	**	1.2	**	**	**	**	**	**	4.2
Hydrazines & hydrazides	19	Methyl hydrazine	0.9	0.8	**	**	**	**	**	6.1	77.0	1.3
Ketones	20	Methyl isobutyl ketone	1.0	0.9	0.4	1.3	0.7	0.5	3.8	7.6	65.0	5.1
Mitro/nitroso compounds	21	Nitrobenzene	(1.0)	(0.7)	(0.6)	(2.0)	(1.0)	(5.8)	(9.3)	(100.0)	**	**
Organophosphates	22	Malathion	1.3	1.1	0.7	1.9	0.8	0.8	5.3	12.0	89.0	2.9
Oxides, alkylene	23	Propylene oxide	0.8	0.8	0.4	1.1	0.7	0.7	5.2	8.7	79.0	4.6
Peroxides	24	alpha,alpha-Dimethylbenzylhydroperoxide	1.1	1.1	0.8	1.7	0.9	1.0	10.5	11.3	93.0	1.6
Phenols & cresols	25	Cresol	1.3	1.1	0.8	2.0	0.9	0.9	**	12.3	100.0	5.6
Sulfates & sulfites	26	Dimethyl sulfate	1.3	1.4	0.6	2.3	1.1	1.0	6.3	10.4	112.0	2.1
Sulfides & mercaptans	27	Carbon disulfide	1.3	1.4	0.8	1.9	1.0	[1.0]	6.0	9.4	119.0	12.1

* The reported preference index data are unitless and were determined from sorption capacity data measured experimentally in the laboratory except as noted:

() = estimated value
[] = literature value

** = Preference index data are not reported for those sorbent/hazardous liquid pairs determined to be incompatible or non-wetting or for which no data exist (see Table B1).

LEGEND:

CLP = Cross-Linked Polymer
D = Diatomite
EM = Expanded Mineral
FG = Foamed Glass
PE = Polyethylene
PP = Polypropylene
PU = Polyurethane
SC = Sorbent Clay
TWF = Treated Wood Fiber
WF = Wood Fiber

sorbent. The preference index provides an indication of a sorbent's performance in a waterspill scenario. The larger the hazardous liquid/water preference index, the greater the hydrophobic quality of the sorbent and the greater the likelihood that it will preferentially sorb hazardous liquid instead of water in an aqueous medium.

Section C - "Technical/Logistical Information"

This section presents guidance on equipment and techniques to use for: 1) the application and collection of sorbents in a spill cleanup situation, 2) the immobilization by sorbents of hazardous liquids for disposal in a landfill, 3) reuse of sorbents, and 4) the disposal of used sorbents. The text describes equipment and manpower requirements, limitations, and safety precautions for the application and collection of the three basic sorbent forms: 1) particulate, 2) pillow, pad, or mat, and 3) sorbent booms.

Section D - "Cost Estimation Procedures And Data"

This section provides data for estimating the cost of using a sorbent. A discussion of general cost categories for cleanup with sorbents is presented. The major categories are equipment, expendable materials, labor, disposal, and transportation. Cost data are given in 1983 dollars for estimation purposes. Guide Sections B and C should be consulted to determine specific equipment, materials, labor, disposal, and transportation requirements.

Section E - "Test Methods"

Section E describes test methods available for evaluating sorbent performance characteristics such as sorption capacity and release rates. Brief descriptions of the test methods, including purpose, applicability, limitations, and data and resource requirements are provided. These sorbent test methods

are discussed in the Manual to enable selection of an appropriate test method if required. Manufacturers' data on sorption of hazardous liquids by sorbents generally do not cite test procedures. The absence of sorbent performance data derived from a common test method makes comparison of results difficult. The test methods cited were developed by the American Society for Testing and Materials (ASTM), General Services Administration (GSA), Westinghouse Corp., Rensselaer University, U.S. Coast Guard, Environment Canada, and Environmental Monitoring and Services, Inc. (Combustion Engineering).

Section F - "Spill Scenario Rationale"

Section F presents the rationale for selecting and defining the four cleanup scenarios considered in this Manual: 1) spills onto land, 2) floating spills into water, 3) non-floating spills into water, and 4) disposal in landfills. These scenarios represent situations where sorbents are likely to be a viable method of spill treatment.

Section G - "Sources of Information"

Sources of information on CERCLA liquids and sorbents are presented in Section G. References such as reports, handbooks, publications, and vendors are identified.

Section H - "CERCLA Liquid Chemical Information"

Section H presents physical property data on specific gravity, solubility in water, viscosity, and surface tension for the CERCLA liquids. The physical data tabulation enables identification of CERCLA liquids with similar physical properties, which is useful information for estimating sorption capacity for similar liquids. The hazardous liquid specific gravity, in conjunction with sorbent specific gravity and sorption capacity, can be used to calculate the

volume of loaded sorbent that will be generated and will subsequently require disposal. The data are organized alphabetically by chemical class followed by the hazardous liquid CERCLA name and the CAS Registry number.

CONCLUSIONS

A Guidance Manual for the Selection and Use of Sorbents for Liquid Hazardous Substance Releases, which is nearing completion, provides a concise compilation of information and data pertaining to the selection, acquisition, application, collection, regeneration, and disposal of sorbents. The inclusion of a chemical index (by chemical name and DOT number), which is cross-referenced to "Sorbent Selection and Use Guides" and "Sorbent Data Sheets," enables the user to quickly locate pertinent sorbent information for the liquid hazardous substances addressed in the Manual. The Manual includes 190 sorption capacity measurements that were made as part of the project and which were unavailable in the literature prior to this effort. The availability of a condensed source of information on sorbents promotes their efficient use by assisting decision-makers to estimate and compare the effectiveness and cost of various sorbent-use strategies. Although the primary target audience for the Manual is Federal On-Scene Coordinators and their technical support staffs, the Manual is also applicable to the needs of spill clean up managers representing State and local agencies as well as the private sector.

REFERENCES

Herrick, E.D., D. Carstea, and G. Goldgraben. Sorbent Materials for Cleanup of Hazardous Spills, EPA-600/2-82-030, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1982.

REVERSE OSMOSIS FOR CLEAN-UP OF SPILLED
WOOD PROTECTION SOLUTION

J.B. Straforelli Pacific and Yukon Region
H. Whittaker EETD

Environmental Protection Service
Department of the Environment

Introduction

General

The wood protection industry uses chlorophenol products, specifically tetra and penta chlorophenols to improve the marketability of the lumber. Since these products are very toxic to aquatic organisms, a B.C. Chlorophenate Wood Protection Task Force has just published a "Code of Good Practice" for the design and operation of wood protection facilities. One of the problems encountered by the task force was the lack of proven technology to clean-up the excess contaminated run-off waters, in order to meet the guideline proposed of 100 ppb, total tetra and penta chlorophenols.

This problem of treatment of effluents containing dissolved toxic materials has been studied for the last few years by the EPS Technical Services Branch, and one of the technologies which has shown good promise is Reverse Osmosis (RO).

The objective of this report is to assess the technical feasibility of using RO to treat chlorophenol contaminated waste waters.

Reverse Osmosis Technology

General

Osmosis is often defined as the ability of a dilute solution to pass through the wall of membrane to dilute the concentrated solution on the other side (hence osmotic pressure is the height or head pressure resulting from the dilute pushing up the concentrate until equilibrium is achieved). Reverse osmosis is simply the process of achieving sufficient hydrostatic pressure to overcome the concentrate osmotic pressure (Figure 1). The use of manufactured membranes (rather than biological or organic membranes) has resulted in applications specific systems.

The manufactured membrane for reverse osmosis permits separation of suspended and dissolved solids in the feed stream which are rejected and remain in large part on the concentrate side. Water and a small portion of the dissolved solids cross the membrane, or permeate, resulting in de-watering, demineralization and water purification.

Mobile Reverse Osmosis

The EPS mobile reverse osmosis unit (Figure 2) is a completely self-contained helicopter transportable, trailer mounted unit. It is powered by a Lister ST2 diesel engine and generates its own 12V DC and 110V AC power for lighting and controls. The "heart" of the unit is the reverse osmosis subsystem consisting of 2 sets of 5-25 micron pre-filters, 2 high pressure pumps, and 2 parallel sets of 3 pressure vessels in series, each containing 2 RO membranes. The basic configuration of the membranes and their installations in the pressure vessels are shown in Figures 3 and 4, respectively. The membranes are of a spiral wound construction and made of thin film composite material.

Operation of the unit is as shown in Figure 5. The main pump feeds the solution through the prefilters to the high pressure pumps. These pumps feed the solution at a pressure of 350 to 7000 kPa (50 to 1000 psi) to the membranes. A system of valves allows isolation of permeate flows at 4 of the membrane sets so that sampling and flow rate determination of the permeate may be carried out. Further valving allows a portion of the concentrate from the two membrane banks to be fed back to the high pressure pump inlet where it is mixed with the incoming feed. This allows varying ratios of permeate to concentrate to be achieved (concentration ratio).

Description of the Problem

In October 1983, during a heavy rainfall, the lumber dip tank at Lynnterm, the Western Stevedoring Company export terminal in North Vancouver overflowed. The spill, which was diluted by rain and wash water was contained and pumped into 6 railway tank cars. Total volume was in excess of 225,000 litres with concentration varying from 100 to 2200 ppm expressed as total chlorophenols. Although primarily containing penta and tetra chlorophenates with sodium tetraborate as a stabilizer, the spilled liquid probably contained wood extracts, sawdust and other fine debris.

A second spill occurred in February 1984 at Cloverdale Paint and Paper in nearby Cloverdale, B.C. In this instance over 45,400 litres of solution was spilled with most flowing into Hyland Creek from there into the Serpentine River. The solution contained sodium tetra and penta chlorophenate, and paraffin waxes. As a result, a substantial fish kill occurred. Although 90 percent of the spilled chemical reached the creek and river, 4500 litres was contained in a ditch on the property. Subsequent rains increased this volume to 68,000 litres, stored in 4 tanks, with chlorophenols concentration varying from 3 ppm to over 700 ppm.

In March 1984, the EPS mobile reverse osmosis (RO) unit was sent to British Columbia to determine the applicability of this technology to the cleanup of spilled chlorophenate solutions. At this time, over 180,000 litres of the chlorophenate contaminated water remained at Lynnterm and 68,000 litres at Cloverdale. Before the trial was complete, surface run-off increased these figures substantially.

Evaluation Program

Lynnterm Trial

The first trial was run on contaminated waste waters containing 510 ppm of chlorophenols. After one hour of conditioning of the membranes, the pressure was increased to 5600 kPa (800 psi). The very dark concentrate and clear permeate were pumped to separate tank trucks. This procedure was continued for 4½ hours, then the unit was shut down and the inlet hose switched to a tank car containing 2055 ppm of chlorophenols. Processing of the waste water from this tank car continued for 4½ hours. The analytical results from samples taken during the first day are shown in Table 1.

TABLE 1

FIRST DAY RESULTS OF WOOD PROTECTION SOLUTION TREATMENT BY REVERSE OSMOSIS - LYNNTERM SITE

Treatment Rate 34-38 litres/minute (9-10 USGPM)

<u>CONCENTRATIONS (ppm)</u>			<u>REMOVAL EFFICIENCY</u>
<u>Feed</u>	<u>Concentrate</u>	<u>Permeate</u>	<u>(%)</u>
510	1062	0.0145	99.997
1655	4042	0.023	99.998

At the end of 2 days of operation (17½ hours), approximately 41,420 litres of solution has been converted to 21,850 of permeate which was dumped into the harbour and 19,570 litres of concentrated solution which was returned to the system for use as make-up feed.

On the third day of operation the unit was run for 1 ¾ hours on the 510 ppm chlorophenol solution then demonstrated to representatives from the B.C. forest industry, private consultants, and government agencies. After the demonstration the membranes were flushed with permeate and then the unit was moved to Cloverdale for a trial on the recovered chlorophenolate solution, and contaminated runoff waters. The unit was used at Cloverdale for six days and was then returned to Lynnterm where it proved capable of processing 100,110 litres of wood protection solution over a seven day period while producing 49,650 litres of concentrate and 50,460 litres of permeate with at least 99.2 percent of the chlorophenols removed.

It was then decided to expand the trial to include two other manufacturer's membranes for comparison. Four Filmtec FT30 and four Desalination Inc. DSI 441 membranes were installed in the unit in place of eight of the Toray membranes. The unit was run at Lynnterm for 10 days processing either the chlorophenol contaminated water or, where necessary, the permeate from the first RO treatment of the effluent. During this period, 117,700 litres of the contaminated water was treated to yield 47,200 litres of permeate and 70,500 litres of concentrate. A substantial difference in performance among the three membranes was apparent during this trial. The

flux rates for all three decayed with time but at different rates. The flux was, however, always better for the FT30 than the DSI 441 which was, in turn, better than the Toray SP 110. There was also difference in rejections. The FT30 was better than the SP 110 which was better than the DSI 441. In all cases, however, except when a mechanical problem occurred, the rejection exceeded 99.7 percent. Summaries of the results for flux rates and rejections included in Table 2,3 and 4 and Figures 6 and 7.

TABLE 2

TORAY MEMBRANES PERFORMANCE AT LYNNTERM

<u>TOTAL CHLOROPHENATE CONCENTRATION (ppm)</u>		<u>PERCENT REJECTION</u>
<u>Tank</u>	<u>Permeate</u>	
735	0.565	99.9
446	0.280	99.9
368	0.002	99.9
243	0.080	99.9
167	0.093	99.9
156	0.009	99.9
136	1.068	99.2

TABLE 3

RESULTS OF WOOD PROTECTION SOLUTION TREATMENT
COMPARISON OF MEMBRANES PERFORMANCE

<u>TOTAL CHLOROPHENOL CONCENTRATION (ppm)</u>				<u>PERCENTAGE REJECTION</u>		
<u>Tank</u>	<u>Permeate</u>			<u>Filmtec</u>	<u>DSI</u>	<u>Toray</u>
	<u>Filmtec</u>	<u>DSI</u>	<u>Toray</u>			
1900	0.445 (1)	1.567	3.337 (2)	99.9	99.9	99.8
735	0.347	1.159	0.565	99.9	99.8	99.9
638	0.174	0.665	2.791 (2)	99.9	99.9	99.6
567	0.073	1.089	6.230 (2)	99.9	99.8	98.9
567	0.201 (1)	0.996	6.16 (2)	99.9	99.8	98.9
290	0.133	0.178	1.668 (2)	99.9	99.9	99.4
218	0.038	0.261	0.434 (2)	99.9	99.9	99.8
156	0.269	0.402	0.009	99.8	99.7	99.9

- (1) Leak at membrane due to twisted "O" ring
 (2) Damaged membrane

TABLE 4

RESULTS OF TREATMENT OF FIRST PASS PERMEATE
COMPARISON OF MEMBRANES PERFORMANCE

<u>TOTAL CHLOROPHENOL CONCENTRATION (ppm)</u>						
<u>First Pass Permeate</u>	<u>Second Pass Permeate</u>			<u>Percent Rejection</u>		
	<u>Filmtec</u>	<u>DSI</u>	<u>Toray</u>	<u>Filmtec</u>	<u>DSI</u>	<u>Toray</u>
3.27	0.040	0.057	0.024	98.8	98.3	99.3
2.059	0.095	0.031	1.494 (1)	95.4	98.5	27.4
1.064	0.133	0.380	1.000 (1)	87.5	64.3	6.0
0.852	0.027	0.076	0.078	96.8	91.1	90.1
0.604	0.014	0.119	0.096 (1)	97.7	80.3	51.0
0.116	0.008	0.034	0.015	93.1	70.7	87.1
0.106	0.003	N/K	0.017	97.2	N/K	84.0

(1) Damaged membrane

Cloverdale Paint and Paper

Initially the solution processed at Cloverdale was very dilute and it was possible to concentrate it by a factor of six. Table 5 gives results of samples taken on that day.

TABLE 5

FIRST DAY RESULTS OF WOOD PROTECTION SOLUTION TREATMENT BY
REVERSE OSMOSIS - CLOVERDALE SITE

Treatment Rate - 34-38 litres/minute (9-10 USGPM)

Concentration in Feed	2.97 ppm
Concentration in Permeate	10 ppb
Removal Efficiency	99.663%

In a 6 day period at Cloverdale the unit processed approximately 28,700 litres of solution containing 3 ppm to 740 ppm of chlorophenols. During the processing of the more highly concentrated solutions, the permeate flow rate dropped dramatically. This was attributed to wax in the feed. Cleaning removed the wax from the membrane but it was re-deposited within a short period of time. Because of fear of causing permanent membrane damage, it was decided to leave the Cloverdale site and return to Lynnterm. After departure of the Environmental Protection Service unit, a private contractor obtained a smaller RO unit. He was able to successfully treat the Cloverdale spill by first lowering the pH to remove the wax, filter the solution, then raise the pH and treat the slightly alkaline solution. Over 157,000 litres were treated in this manner with 30,000 litres of concentrated solution being recovered for disposal and 127,000 litres of permeate being discharged into the sanitary sewer system.

Reverse Osmosis Coupled with Activated Carbon Technology

As seen earlier, the data indicates that reverse osmosis is an effective method for concentrating chlorophenates but that the desired limit of less than 100 ppb in the permeate could not always be achieved in one pass, and thus it was required to treat the permeate once more. Earlier testing by EPS Burlington Waste Water Technology Centre had shown that granular activated carbon (GAC) would reliably remove high percentages of chlorinated phenols from dilute contaminated water. It was therefore decided to carry out a trial in which reverse osmosis would be used to concentrate the spilled wood preservative and produce a "rough" permeate which would be "polished" by GAC. Approximately 73,000 litres of wood preservative were processed to give equal amounts of concentrate and permeate. The permeate was then fed to a series of three 1.2 m by 10 cm GAC columns and the effluent collected. The results of this combination were spectacular. The contaminated water, which had varying concentrations of 380 to 2000 ppm chlorophenols, when treated by RO gave a permeate with an average of 1.3 ppm chlorophenols. The permeate when treated by GAC resulted in an effluent with an average of 1.7 ppb chlorophenols. (The drinking water standard in B.C. is 2 ppb). Results of this trial are included in Table 6.

TABLE 6

RESULTS OF TWO STAGE PROCESS USING REVERSE OSMOSIS AND GRANULAR ACTIVATED CARBON FOR CLEANUP OF SPILLED WOOD PROTECTION SOLUTION

(Total Chlorophenol Concentration in Feed 380 to 2000 ppm)

TOTAL CHLOROPHENOL CONCENTRATION (ppb)

Reverse Osmosis Permeate	GAC Column		
	1	2	3
1,658	3.42	5.08	1.46
954	5.11	3.84	2.9
1,136	5.8	2.95	3.63
1,801	7.78	4.75	1.17
941	12.07	3.6	0.83
931	4.72	2.74	0.11
895	0.89	1.28	1.42
1,393	2.1	1.4	0.8
1,923	14.7	2.0	2.9

Discussion of Results

Objectives Obtained

The trial was undertaken to assess the capability of reverse osmosis in treating chlorophenolate contaminated waste waters that would require treatment or disposal. Based on previous work, using the same RO unit and membranes of the same type on dilute aqueous solutions for chlorobenzene, rejections of 99.9 percent were expected for the Toray membranes. The early encouraging results (Table 1) were a pleasant surprise.

The membranes used in this trial are designed for the production of fresh water from salt water. Pretreatment is normally required to ensure long life and continuous high permeation rates. The decay of flux rates with time for all membranes does not, therefore, come as a surprise. The fact that they were able to handle the untreated contaminated water for long periods is considered to be a tribute to their design and manufacture. This is especially true since simple flushing with permeate was sufficient to restore performance.

Comparison of the membranes' performance at Lynnterm (Tables 3 and 4 and Figure 5 and 7) demonstrate the high rejection and high permeate flux achievable with the proper membrane. It appears from this data that the FT30 is the best for the purpose.

The average permeate concentration in total tetra and penta chlorophenols obtained with the Filmtec and Toray membranes were 0.2 and 0.3 ppm, respectively, while the average concentration of the contaminated waters treated was 634 ppm. This is not good enough to meet the guideline proposed in the code of good practice, which is less than 0.1 ppm. However the latter could be reached with confidence by reprocessing the permeate obtained from the first RO treatment. Table 5 shows that a second treatment would on the average yield concentrations around 0.03 and 0.04 ppm using either Filmtec or Toray membranes.

The following is a simple comparison of the cost estimates for the disposal of excess contaminated waters. i.e., contaminated effluent which cannot be returned to the process. Assuming 100,000 litres have to be disposed of, the cost for the current method of shipment to a US disposal site would be about \$48,000, whereas the operating cost for a RO system, including the reprocessing of first pass permeate, would be about \$6,500.00. However a capital expenditure in order of \$41,000 would be needed for the purchase of a unit. This investment would be paid back by the treatment of 100,000 litres of excess contaminated water.

The combination of RO and GAC appears to be extremely effective. RO gives very good rejections from very dirty wood protection solutions. It is capable of handling a spilled solution with no pretreatment. GAC, on the other hand, is more effective when the wide ranges in pH and the high solids loading common in a spilled chlorophenate solution are eliminated. It is very efficient for the treatment of a dilute solution such as that found in the RO permeate. The combination allows a spill of chlorophenate solution to be converted to make-up solution for the wood protection dip tank, permeate with residual chlorophenols lower than 2 ppb, and a small amount of contaminated carbon for disposal.

Problems Encountered

The decrease in permeate flow experienced at Cloverdale points to the need to know what is in the solution to be cleaned-up. Fortunately in this case the decrease in flow due to the wax in solution was reversible and was more of a nuisance than a problem. Indeed normal flows were restored by flushing the RO membranes with permeate every six hours. Another improvement brought by the private contractor who completed the clean-up at Cloverdale, was to filter the solution to be processed first through a twenty micron filter and then through a series of cartridges down to one micron. This drastically reduced the fouling of the membranes.

During the trials some leaks were observed due to either twisted "O" ring or damaged membranes. This should not happen in well designed and well run system. However a turbidity detector on the permeate side would allow for the detection of these kinds of operating problems.

Conclusions

This experiment was originally intended to be a short term trial to assess the feasibility of using reverse osmosis to cleanup a spill of wood protection solution. As a result of the interest shown by the management of Lynnterm and Cloverdale Paint and Paper as well as other environmental agencies, it was expanded to become a major operation. The early expectations that RO would prove effective for this purpose were more than fulfilled.

1. Reverse osmosis is an effective method of processing spilled chlorophenates solutions, particularly when high concentrations of total chlorophenols are involved. No other known technology can process wood protection solutions with total chlorophenols in the 3-2000 ppm range and produce an aqueous effluent with only 0.03-0.04 ppm total chlorophenols.
2. The combination of reverse osmosis and granular activated carbon is also a very effective way of dealing with both wood protection spills and runoffs from wood protection processing and storage sites.

Figure 8, shows a block diagram of a possible industrial installation using either RO technology alone or combined with GAC.

3. Reverse osmosis is a cost effective method of handling wood protection solution spills.

Acknowledgements

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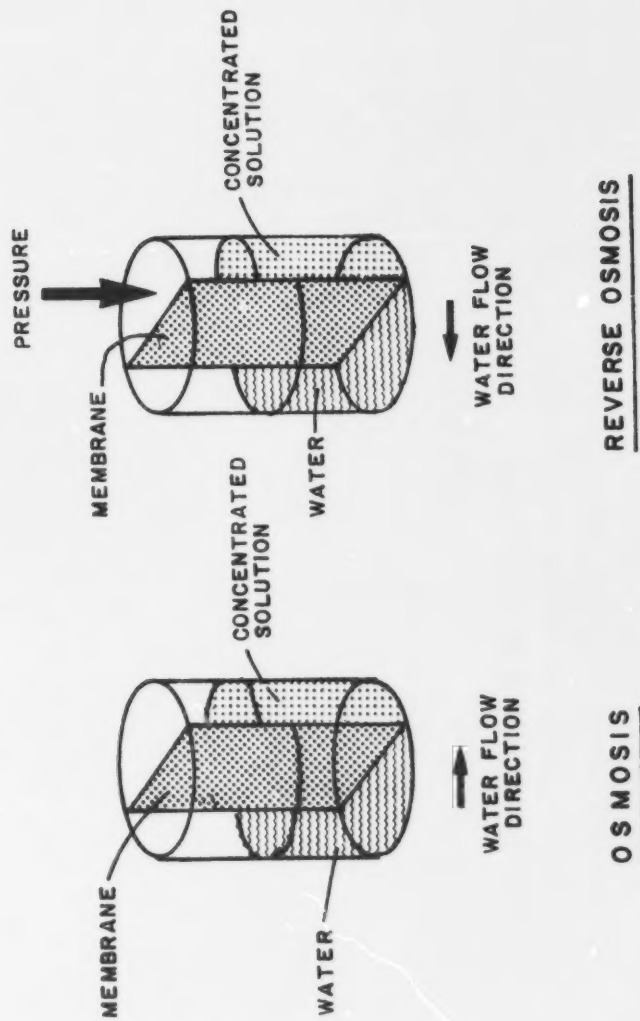


FIGURE 1 REVERSE OSMOSIS

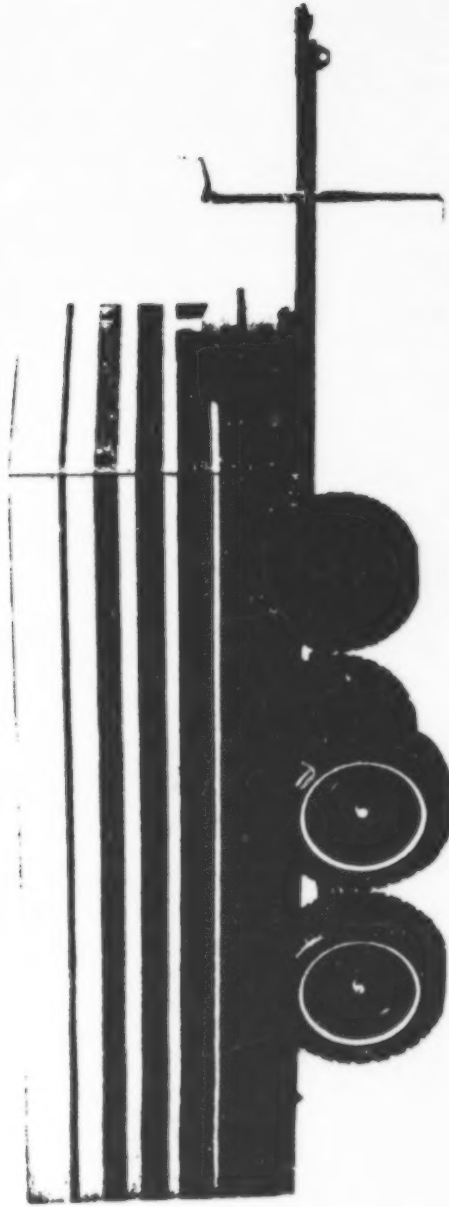
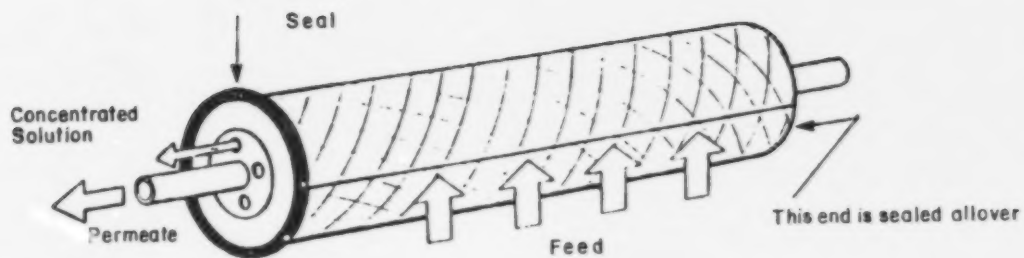
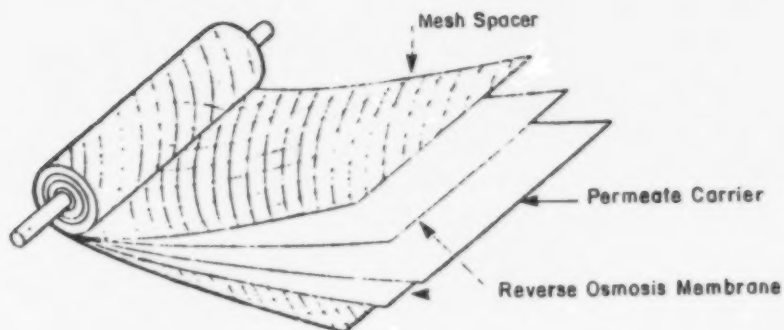


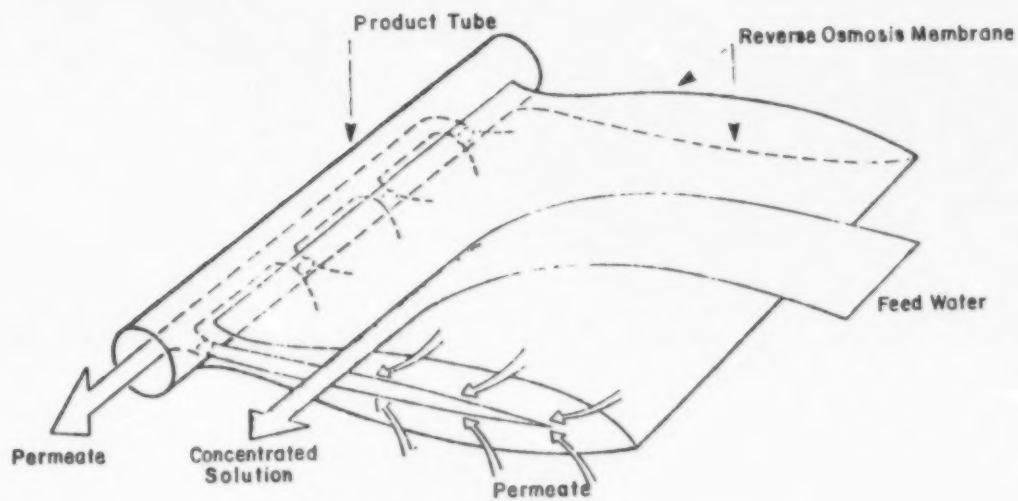
FIGURE 2 EPS MOBILE REVERSE OSMOSIS UNIT



EXTERIOR VIEW OF MODULE AND DIRECTION OF FLOWS



MATERIALS OF MODULE



DIRECTION OF FLOWS

FIGURE 3 BASIC CONFIGURATION OF MEMBRANES

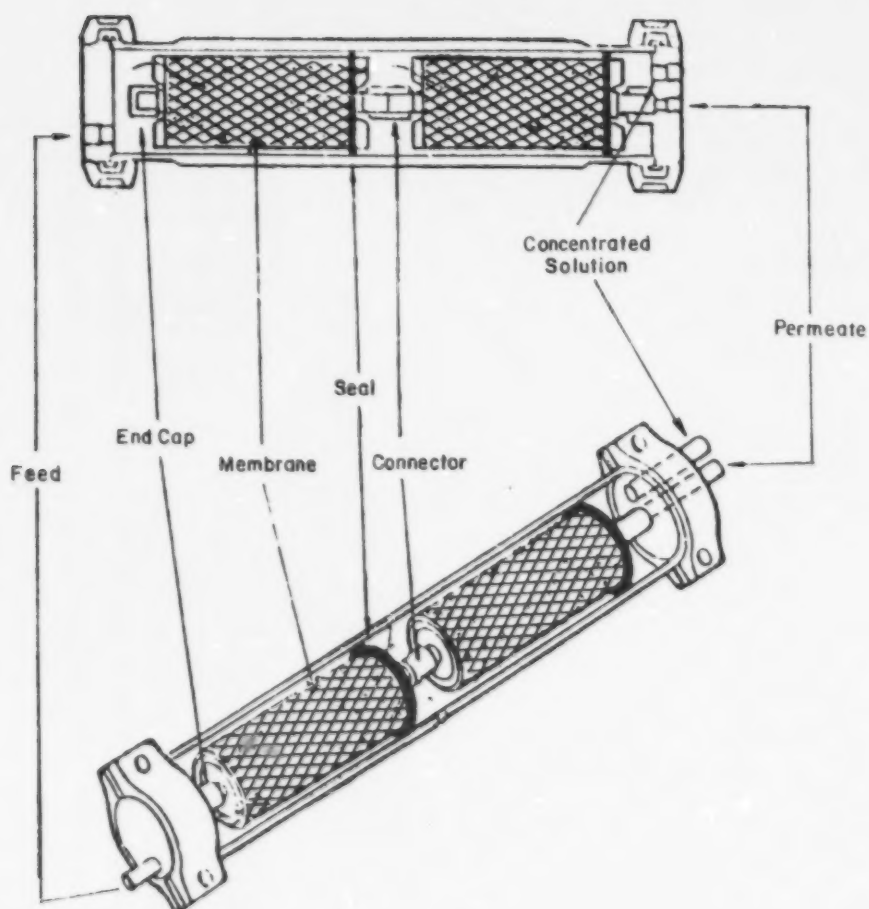


FIGURE 4 MODULE PACK ASSEMBLY IN A PRESSURE VESSEL

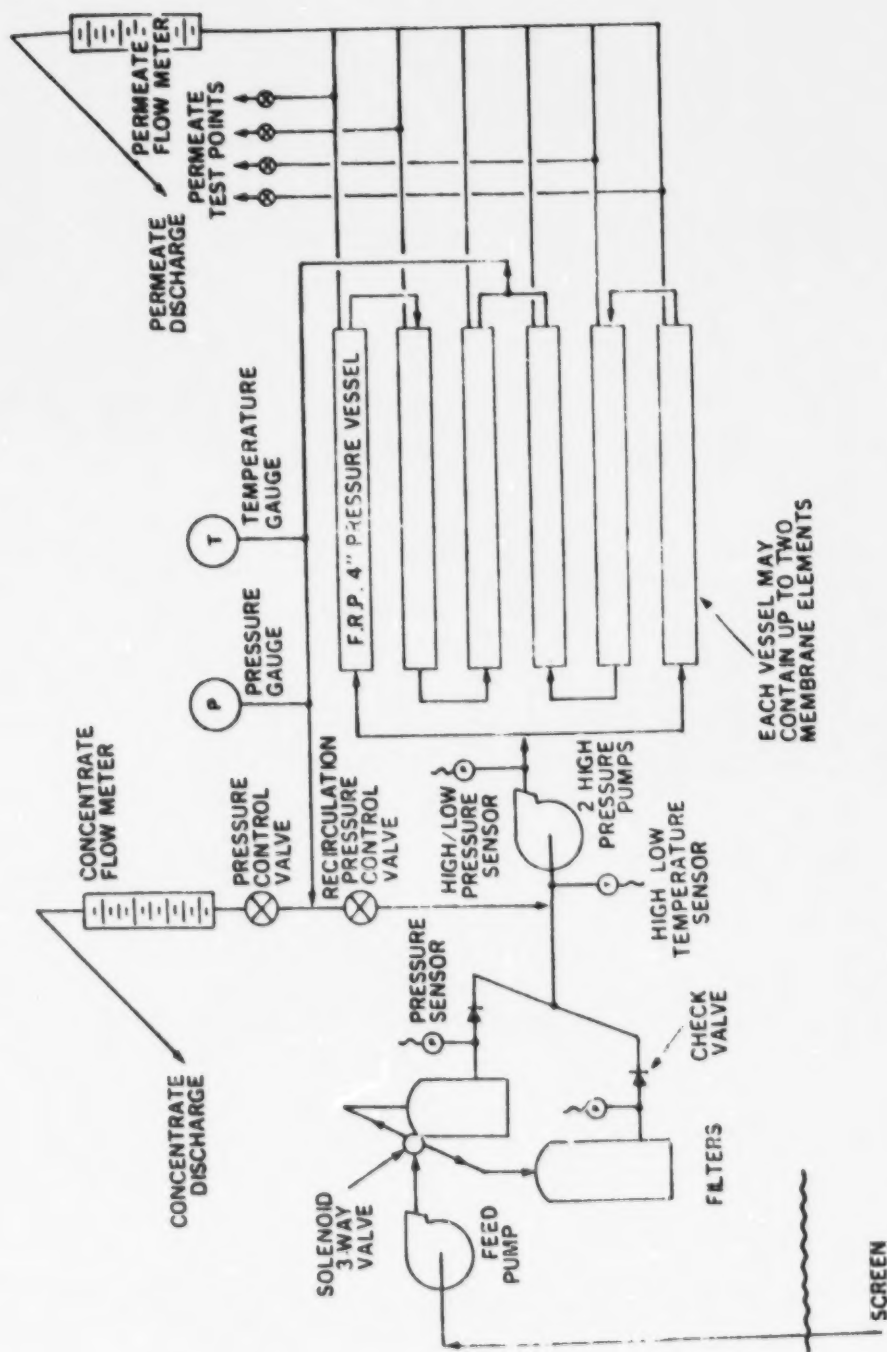


FIGURE 5 SCHEMATIC OF RO UNIT OPERATION

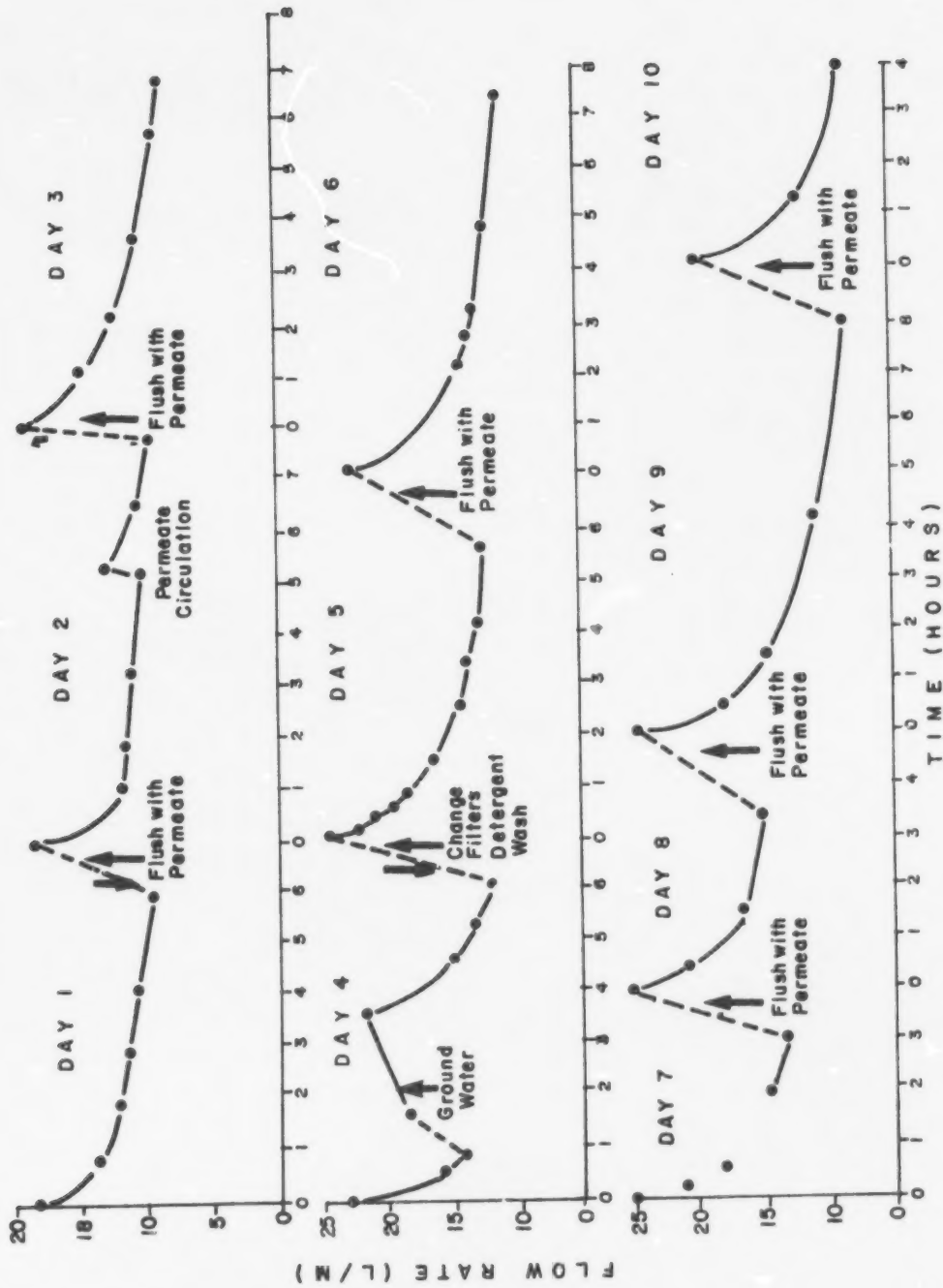


FIGURE 6 PERMEATE FLOW VERSUS TIME - TWELVE TORAY MEMBRANES - LYNNTERM

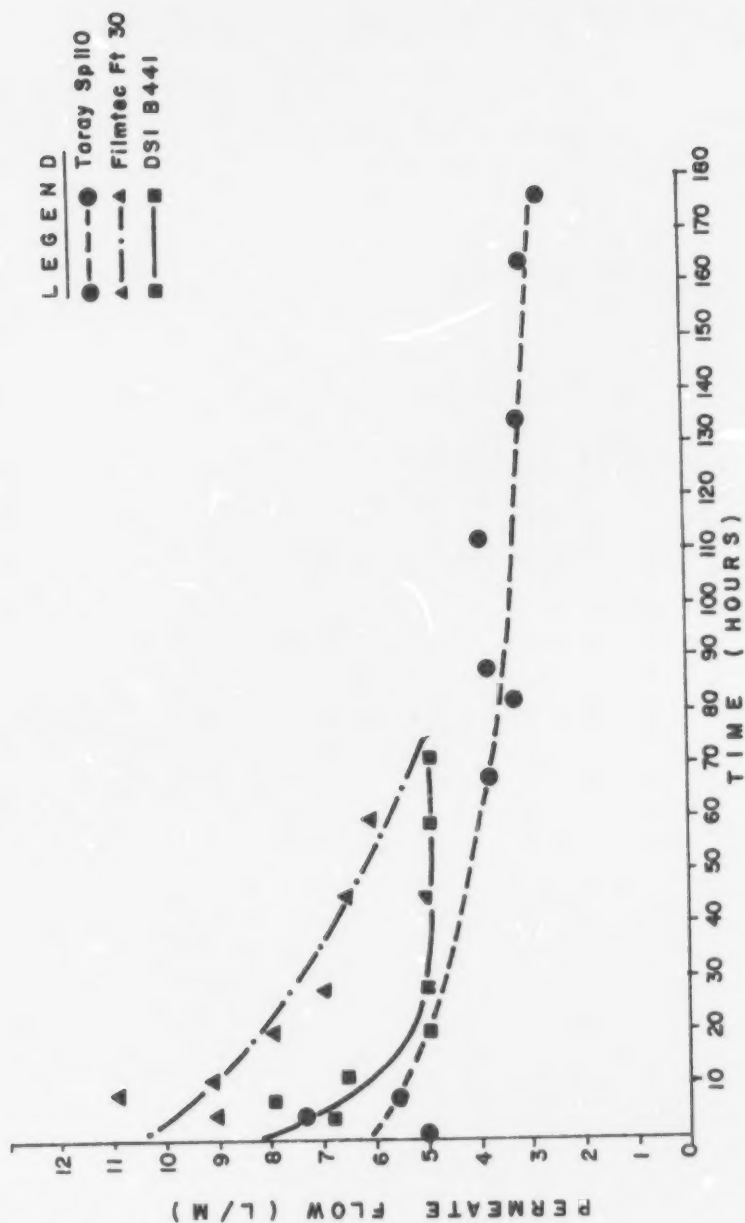


FIGURE 7 PERMEATE FLOW VERSUS TIME - FOUR MEMBRANES - LYNNTERM

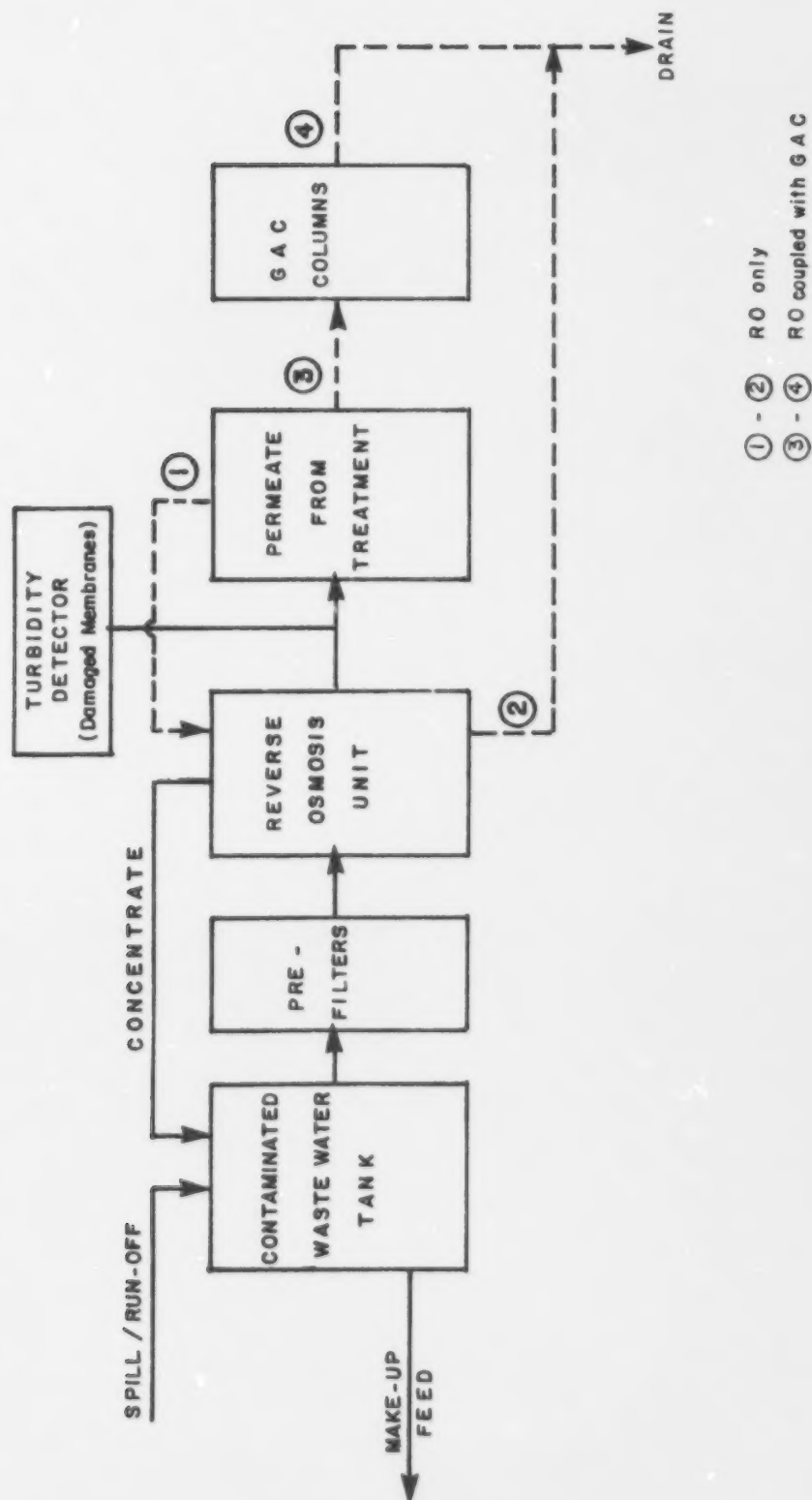


FIGURE 8 INDUSTRIAL INSTALLATION FOR TREATMENT OF RUN-OFF WATERS AND SPILLS

APPLICATION OF INDUSTRIAL HYGIENE TECHNIQUES DURING AN EMERGENCY RESPONSE
OPERATIONS AT WESTERN PROCESSING COMPANY, INC., KENT, WASHINGTON

Rodney D. Turpin
Safety & Occupational Health Manager
U.S. Environmental Protection Agency
Environmental Response Team
Edison, New Jersey

Jim Willman, On-Scene Coordinator
and
Ron Blair, Regional Safety Officer
Region X Office
U.S. Environmental Protection Agency
Seattle, Washington

INTRODUCTION

In 1980, Congress enacted the Comprehensive Environmental Response Compensation and Liability Act, (CERCLA), commonly referred to as "Superfund". Today, Superfund permits the Federal government to work with State and Local governments to provide immediate and comprehensive response to the release of hazardous substances.

It is not the intent of this paper to deliver EPA's policy or discuss the development of such policy. Instead, the objective is to address the Western Processing Company, Inc. (WPC), Kent, Washington clean-up activities from an Occupational Health and Safety Professional's viewpoint and demonstrate how the U.S. EPA, OERR, HRSD's, Interim Standard Operating Safety Guides, Sept. 1982 is used to develop an operational Site Safety Plan. WPC was not the largest EPA clean-up activity for 1983, but it does demonstrate how rapidly a

"Safe" clean-up activity can be undertaken at a very complex site. WPC is approximately a 13 acre recycling facility involving halogenated and nonhalogenated solvents, plating wastes, and other potentially toxic materials. The site is located inside a large industrial area and contains 70 storage tanks, 55-gallon drums, lagoons, etc. In short, this response highlighted such industrial hygiene techniques as respirator selection, heat stress monitoring, air sampling, and decontamination - just to mention a few.

BACKGROUND

In 1981, the initial site survey revealed the presence of approximately 2,900 drums containing a wide variety of materials. It also revealed six storage/drying lagoons for acids/caustic/paint wastes, a storage/drying lagoon for fertilizer, 10,000 tons of flue ash, 8,000 tons of battery chips, solvent recovery plant with storage/tank area, 70 bulk storage tanks, 5 cooling water lagoons, chlorine gas tank storage house, and a small laboratory.

A total of 87 priority pollutants were identified in the soil and groundwater on the site. In addition, soil samples from the site revealed the presence of organic compounds at levels of less than 10 ppm. (e.g. acetone, MEK, MIBK, 2-pentanone, 2,4-dimethylcyclobutenone, ethylbenzene, xylene, toluene, trichloroethylene, 1,2,3-trimethylcyclohexane, tetrachloroethylene, 2-methyl 1-pentene, methyl cyclohexane, ethyl cyclohexane).

Inventory records and drum labels indicated the presence of hydrochloric acid, nitric sulfuric chromine, phosphoric and hydrofluoric acids, sodium hydroxide, formaldehyde, trichloroethylene, ink, acetone, freon, methyl ethyl ketone, isopropyl alcohol, zinc oxide, perchloroethylene, methanol, xylene, methylene chloride, toluene, etc.

As is common with hazardous waste sites, one must have reservations about all available data especially obtained from inventory records and drum labels. Also, one cannot rule out the fact that additional materials may be present or drums/tanks, etc., exist in an unstable condition.

Thus, the task before the on-scene coordinator (project engineer) is how to handle the unknown wastes as safely and expeditiously as possible. The OHSP's job is just as difficult since he/she must evaluate every phase of the proposed operation and all the plausible options. The OHSP must utilize every portion of his/her multidisciplinary training to assist/advise the on-scene coordinator of the safest containment, remedial, etc., action for present conditions as well as address the potential factor of the worst case situation (fire, explosion, etc.) At the Western Processing Company, the OHSP's were primarily responsible for developing/implementing on-site activities. Some of them were:

1. Site safety protocols
2. Health/safety enforcement
3. Sampling procedures (e.g. drums, lagoons, tanks, etc.)
4. Waste compatibility testing
5. Air sampling plan

As you can see, the OHSP is required to work side-by-side with site operational personnel (such as: engineers; chemist; biologist; transportation and site logistics personnel.) In short, he/she becomes an active part of the operational unit advising the on-scene coordinator before/during every potential operation phase. This operation role, which he/she is often not acquainted with in a traditional occupational setting, requires the Occupational Health and Safety Professional to wear two basic hats - Assistant Site Engineer and Health/Safety Officer.

The following briefly describes the OHSP's involvement with operational phases mentioned above.

Site Safety Protocols

Relying on their multidisciplinary training, site experience, and EPA, OERR's Sept. 1982 Interim Standard Operating Safety Guides, the OHSP's developed, implemented, and modified a site specific safety plan which addressed all phases of the clean-up activity.¹ The Site Safety Plan addressed the following major points:

1. Identify key personnel and alternate responsibilities.
2. Identify specific risk associated with site tasks.
3. Identify level of protection to be used per specific site tasks based on potential exposure.
4. Designate work areas.
5. Identify personnel task in work zone during staging, operation, etc.
6. Designate equipment and associated physical hazard tasks on-site.
7. Compatibility testing tasks.
8. Site emergency procedures in case of fire, explosions, etc.
9. Designate air monitoring requirements.
10. Identify necessary training.
11. Designate site access/control as well as security procedures.
12. Decontamination requirements.
13. Identify employee monitor requirement e.g., medical exams, heat stress, etc.

Health/Safety Enforcement

While the OHSP is part of the operational engineering work unit, he/she must also make sure that "all" site personnel are adhering to the Site Safety Plan and the plan is updated as required. On this specific response, the enforcement role was conducted by the U. S. Coast Guard, Pacific Strike Team. A USCG safety officer/monitor accompanied each site specific work group and assured site activities complied with the site safety plan.

Sampling Procedures

While the OHSP had an active role in sampling procedures, the majority of the effort was reviewing proposed job objectives and determining the safest way to obtain the objective in the most timely fashion. An example of this active role was demonstrated by the sampling procedures used at the open lagoons and 6,000 gallon storage tanks. The OHSP's presence on-site developed the protocol in conjunction with site sampling personnel. They were able to show that a rental cherry-picker rig would expeditiously and safely allow a sampling over the lagoon waste area and on top of the storage tanks. While other methods suggested addressing sampling with appropriate safety equipment, they overlooked the most common occupational hazards - slips, trips, and falls.

Waste Compatibility Testing

The objective was to characterize the 2,900 drums in order to permit bulking. The OHSP's role here is a major one since he/she must assure that the tests are performed in a timely manner (approx. 200 per day) but that personnel are protected as safely as possible and any accidents (fire, spills, explosion)

incurred during the testing does not react with waste located at the site.² This was achieved by the OHSP's developing a site specific testing protocol, assuring that the proper safety equipment would permit maximum personnel movement and appropriate testing sequence. The tests were conducted outdoors to reduce potential inhalation hazards to personnel wearing respirator protection.

Air Sampling Plan

The tasks before the OHSP is both complex and difficult. He/she must address employee exposure, changes in site vapor/aerosol concentration, changes in weather condition, and effect on nearby ambient conditions. All this must be done when dealing with unknown vapors/aerosols.

The tasks were handled at this site by utilizing equipment ranging from real-time field instruments to off-site GC/MS analysis.³

CONCLUSION

While it is obvious many disciplines are required to make a hazardous site clean-up activity a successful one, we hope this case history helps to demonstrate the multidisciplinary training necessary for the Occupational Health and Safety Professionals. They must not only practice their own profession but be required to eat, sleep, and think like other disciplines required at a hazardous waste site. Yet, they must be self-disciplined in order not to get so involved during the activities that they try to substitute for the on-site engineer, chemist, etc. role.

ACKNOWLEDGMENTS

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HEALTH AND SAFETY AND TRAINING FOR
HAZARDOUS MATERIALS RESPONSE PERSONNEL

Martin S. Mathamel
George M. Crawford

Roy F. Weston, Inc.
West Chester, Pennsylvania

INTRODUCTION

Existing Occupational Health and Safety Administration (OSHA) guidelines as well as recent "Right-to-Know" and "Hazard Communication" legislation within the United States have emphasized the need for management to develop and implement health and safety programs for employees who handle hazardous materials. Although many of these regulations are not completely applicable to personnel involved in hazardous materials response and clean-up, they represent current regulatory intent. Due to implicit liabilities, organizations involved in environmental response operations must not only be cognizant of regulatory intent, but must have the foresight to be state-of-the-art in terms of health and safety. A training program is an integral and extremely important part of any comprehensive health and safety program, and is required by many of the regulations. Workers in manufacturing facilities are relatively easy to train, since the hazards in most industrial settings are well defined; in addition, established regulations and guidelines generally address common industrial workplace hazards. For response personnel, where the workplace is the spill scene or the waste site, the hazards are not clearly defined. In many instances, field activities require the active cooperation of individuals from many different backgrounds. Training programs for response personnel must therefore include instruction in both technical skills as well as in the wide spectrum of hazards associated with hazardous materials field operations, in accordance with the intent of "Right-to-Know" and "Hazard Communication".

For the past several years, Roy F. Weston, Inc. (WESTON) has assisted numerous industrial and government clients in the areas of hazardous chemical spill prevention and emergency response and hazardous waste site investigation and clean-up. Since there is not a single agency, association, or governing body within the United States that has completely defined what elements constitute an integrated health and safety and training program, that satisfies all moral obligations, WESTON has developed a program for its employees. This paper describes the segment of the basic program which is aimed at field personnel.

HEALTH AND SAFETY PROGRAM ELEMENTS

Medical Surveillance

Integral to the health and safety program is medical surveillance. The WESTON medical surveillance program has been designed to serve two purposes. The first is to certify personnel fit to perform hazardous materials field work. This includes certifying individuals to wear respirators as required by OSHA regulations. The second is to provide a means of establishing a medical baseline against which to measure any adverse impact of working with

hazardous materials. Medical surveillance examinations are required for field personnel upon being hired and prior to assignment to field work, annually thereafter, at the time of resignation, or at such times as directed by the Health and Safety Officer (HSO).

The medical surveillance protocol was established based on Company experience with the input of a physician. In order to standardize the program, which must be administered at numerous locations across the country, a medical service was contracted. The service uses a network of pre-screened clinics to perform all tests. The results are sent to a central clinic for interpretation and computerization. The central clinic, in which one physician is assigned as a program monitor, prepares a summary report, which is sent to the HSO at the WESTON Corporate Headquarters. The result of using the service is uniform evaluation criteria.

The examination protocols and their rationale/interpretation are as follows:

<u>TEST PARAMETER</u>	<u>RATIONALE/INTERPRETATION</u>
Vital Signs	General state of health.
Screening Audiometry	Hearing acuity.
Pulmonary Function	Ability to wear respirator.
Resting EKG	Baseline cardiac condition.
Chest X-Ray	Evaluate lung disease.
Blood Count	Evaluate blood forming organs.
Urinalysis	Evaluate kidney/bladder.
Urine heavy metals	Evaluate baseline/exposure.
Blood Lead	Evaluate baseline/exposure.
SMA-24	Evaluate Kidney, Liver endocrine and other metabolic functions.

The Resting EKG is performed for screening purposes. Experience has indicated that there is no advantage to a Stress EKG unless indicated by the Resting EKG results. An SMA-24 normally includes the following: Renal Function (BUN, Creatinine); Lipid Metabolism (Cholesterol, Triglyceride, LDL Cholesterol, HDL Cholesterol); Electrolyte Balance (Sodium Potassium, Chloride, Carbon Dioxide); Acid/Base Balance (Calcium, Phosphate); Protein Metabolism (Total, Albumin, Globulin); Liver Function (Total Bilirubin, Alkaline Phosphatase, SGOT, SGPT, LDH); Iron Metabolism (Serum Iron); and Endocrine/Metabolic (Glucose, Uric Acid). Cholinesterase is not routinely evaluated as it is specific to organophosphate pesticide exposure and has not real meaning in a baseline scan.

Personnel are briefed as to the meaning of the individual test parameters, how adverse exposure effects test results, and how test results are

used by the Corporation. Implicit in OSHA regulations is that personnel must be informed if they are suffering adverse health effects as a result of field exposure.

The medical surveillance program also includes a contract medical emergency service which provides 24-hour consultation for emergency medical problems.

Corporate/Regional HSOs

The health and safety program includes regular administration of health and safety policy via a network of Corporate and Regional HSOs. A health and safety plan is required for all field activities. The plans are approved either at the regional or corporate level by the HSO; as appropriate. Regular meetings are held between the various HSOs; the meetings are supplemented by monthly telephone conference calls. The meetings and conference calls serve as a forum to discuss health and safety related topics and problems. The HSOs are also responsible to insure that all safety equipment is maintained in the proper condition; this responsibility is normally delegated to a Corporate/Regional Equipment Officer.

Exposure/Accident Reporting

Key to the health and safety program is the exposure/accident reporting system. Any exposure/accident that may effect the health and safety of any employee is reported to the HSO by utilizing a standard form developed specifically for hazardous materials field operations. This system allows the HSO to monitor the suitability of employee for field work.

Quality Assurance/Quality Control (QA/QC)

As in all types of business, quality assurance and quality control are of utmost importance in maintaining an effective safety and health program. WESTON'S QA/QC procedure regarding the Health and Safety Program includes program and field site audits, review of safety plans by individuals not intimately involved in a project, and appointment of an overall Quality Assurance Officer at the corporate level. The QA/QC program is a Standard Operating Practice (SOP), allowing it to be uniformly implemented company wide. Health and Safety and Training is part of the QA/QC program.

TRAINING PROGRAM ELEMENTS

Prior to assignment to hazardous materials response activities, personnel must complete a three day training session which serves to introduce basic health and safety concepts, and meet the Corporation's liabilities under OSHA. Upon completion, employees are given field assignments based on prior experience as well as the judgement of the HSO. Inexperienced personnel are gradually introduced to hazardous materials field activities, making their initial field visits with experienced personnel.

Remedial Response Health and Safety Training Course

The agenda for the three day WESTON Remedial Response Health and Safety Training Course (RFW 1180.3) is as follows:

Day 1

Hazard Recognition and Evaluation (2 hours)
 Toxicology (1 hour)
 Exposure Guidelines (1 hour)
 Sources of Information (1 hour)
 Monitoring Instruments (2 hours)
 Homework Assignment: Hazard Recognition and Evaluation

Day 2

Discussion of Homework Assignment (1 hour)
 Levels of Protection (1 hour)
 Protective Clothing (1 hour)
 Air Purifying Respirators (APRs) (1 hour)
 Self-Contained Breathing Apparatus (SCBAs) (1 hour)
 APR/SCBA Field Exercise (includes Fit Test) (2 hours)

Day 3

Site Safety Plan (1 hour)
 Site Control and Decontamination (1 hour)
 Hazardous Material Sampling (1 hour)
 QA/QC/Legal Considerations (1 hour)
 Hazardous Materials Response Field Simulation (3 hours)

The subject matter of each individual agenda item is discussed below.

Hazard Recognition and Evaluation

Field personnel are routinely exposed to a variety of physical and chemical hazards. OSHA regulations mandate that personnel be able to recognize these hazards. Instruction in this area dwells on recognition by stressing thinking before reacting; common sense is the key. Management's position in terms of taking risks to get a task completed on time and within budget is stressed. The bottom line is if personnel feel unsafe, the task is to be delayed until a sound approach has been devised. The costs of implementing alternative approaches are usually a mere fraction of the cost of accidents. On the other hand, response and clean-up operations involve a certain amount of risk. In fact, unnecessary caution may jeopardize the well being of other field personnel. The key is in educating personnel to be rational in their approach to hazards.

Physical hazards include thermal, mechanical, electrical, and noise related exposure. Instruction on the hazards most likely to be encountered is required, including hazards expected at construction work sites. Chemical hazards include combustible, explosive, toxic, corrosive, and reactive materials. Instruction in basic chemical principles (combustion, reaction, thermal properties, etc.), the significance of physical/chemical parameters (BP, MP, solubility, density, vapor density, pH, flash point, fire point, etc), and the practical considerations in dealing with chemical hazards in the field is basic to hazard recognition. In all cases, merely defining the hazard/parameter is not sufficient. The significance of the

hazard/parameter in field operations is of importance.

Toxicology

The importance of instruction in classical toxicology is a subject of debate. While it is true that an LD₅₀ (Lethal Dose 50) and similar data is usually of minimal help in determining exposure guidance in the field, toxicological data is nonetheless the basis for many of the exposure guidelines currently in use. A discussion of classical toxicology definitions and such topics as carcinogenicity, mutagenicity, teratogenicity is included. What is stressed are the practical aspects and how the various parameters effect field operations. Routes of exposure, acute and chronic reactions, synergism, antagonism, duration and frequency of exposure, and toxicity classifications are the key.

Exposure Guidelines

Exposure guidelines for toxic hazards include the PEL, the TLV, the BLV, the IDLH concentration, the MEG and the CAG for both short and long term exposures of field personnel and members of the community. For explosion hazards, action levels based on the LEL/UEL concentrations are stressed. Several Federal agencies have developed guidelines for radiation, heat, and noise exposure. Personnel are instructed in the source and the implications of the various exposure guidelines. This is relatively easy in the case of guidelines which have been adopted by the law or by accepted practice. However, many guidelines are recommendations that may or may not be adopted in individual organizations. Special circumstances may warrant adopting them on a case by case basis, with specific monitoring procedures. Usually this requires the input of the HSO; therefore, the mechanism of accessing the HSO is clearly stated. In all cases it is stressed that exposure guidelines are based on assigning safety factors to the expected reaction of "normal" humans under "normal" conditions; field conditions may drastically alter the guidelines. The key here is educating personnel to recognize when they need an expert to develop new guidelines, and when they can rely upon preestablished ones.

Sources of Information

Personnel need access to a wide variety of technical literature in order to safely perform field activities. There are numerous technical publications from the USEPA, NIOSH, OSHA, NEPA, USCG, etc., as well as several good computer access systems, such as CHEMPREC, OHMTADS, CHRIS and others. A presentation detailing the advantages and limitations of the major sources of response information is presented.

Monitoring Instruments

Field personnel use monitoring equipment to characterize sites, determine level of protection, estimate community impact, etc. Instruction in the use of available equipment is provided. The key is the realization that not all individuals should be expected to use all of the equipment; nonetheless, personnel should be aware of what types of equipment are used to determine different hazards. A tiered approach is highly recommended. Equipment that is relatively easy to use and interpret include the Combustible Gas Indicator/Oxygen Meter (explosion/O₂ deficiency hazard), the Radiation Survey Meter (Radiation hazard) the² Colorimetric Detector Tube (toxic hazard), the pH meter (corrosive hazard), passive monitors/dosimeters

(various hazards) and similar equipment. In most cases, individuals can easily be taught the basic operating procedures for this type of equipment.

More difficult are the commonly available Total Vapor Detectors (TVDs) for determining toxic hazards such as the portable Photoionization Detector (PID) and Flame Ionization Detector (FID). Extremely difficult is the portable Gas Chromatograph (GC), Infrared Detector (IR), the Programmed Thermal Desorber (PTD), and sampling pumps and collection media for toxic hazard determination. Standard operating procedures, calibration and maintenance are stressed. Data reporting and interpretation is extremely important, as well as action levels based on exposure guidelines. The individual(s) within the company in charge of implementing monitoring programs and maintaining the equipment are clearly identified.

Levels of Protection

The USEPA, the USCG, and other Federal agencies have adopted a comprehensive system for specifying what type of protective gear is to be worn in the field based on a selection protocol. This system establishes four levels of protection: Level A, B, C and D. The equipment that is used for each level and selection criteria is discussed.

Protective Clothing

Several OSHA regulations, ANSI standards and NIOSH publications detail specifications and selection criteria for protective clothing. Personnel are made aware of these standards, and how they impact selection of protective clothing. The requirements for selection (strength, flexibility, temperature, chemical and aging resistance, and cost) are presented as well as the basic concepts of penetration, degradation, and permeation. Different construction materials and their trade-offs are discussed. The bottom line, however, is a discussion of the basic gear that personnel are being provided, its uses and limitations. Maintenance, storage, and disposal are likewise important, including guidelines for determining when the clothing is no longer usable.

Respiratory Protection

OSHA regulations establish the minimum requirements of a respiratory protection program. Training is integral to the program. The standards state definite training requirements, requiring instruction on the overall program as well as on each individual piece of respiratory gear supplied to the employee, on a continuing and regular basis. At a minimum, the instructions must be written. WESTON personnel are instructed on the use of an SCBA(s), APR(s), and escape mask(s). Part of this instruction is cleaning and maintenance and troubleshooting, i.e., how to recognize and correct equipment failure in the field. In addition, the training program includes a session on the theory of respiratory protection, selection criteria, and physiological and psychological restrictions. The field exercise consists of a full dressout, and participation in mildly stressful exercises that attempt to simulate field conditions. The respiratory training likewise includes a qualitative fit test to determine the suitability of the gear on each individual.

Site Safety Plan

The use of site safety plans cannot be overemphasized. The safety plan and the site control plan are often combined. Good safety planning is an art that can only be learned with experience; however, there are simple basic concepts that are presented. The site safety plan

designates all of the equipment and procedures to insure the safety of the team, and serves as a checklist that aids in the implementation of site work activities. All emergency information (hospital, ambulance, fire, police, spill control, etc.) is included. What is important is for all personnel to have a thorough understanding of what is to be done, the sequence in which it is to be done, and the individuals who are responsible to do it.

Site Control and Decontamination

Critical to the safe and cost-effective completion of field activities is site control and decontamination. Although each different site will have a unique approach, uniform procedures are emphasized. A standard format for a site control plan is presented. The responsibilities of the Team Leader, the Equipment Officer, the Safety Officer, and the Work party are discussed in detail. A discussion of community relations and interaction with the news media and other site personnel, such as construction workers is included. Personnel and equipment decontamination is critical if health and safety is to be maintained. Detailed procedures are presented. Of importance is how contaminated clothing and wash solutions are to be treated and disposed of. Emphasis is on tailoring the decontamination procedures to the individual site, and the use of common sense. Avoidance of contamination and good work practices is stressed.

Hazardous Materials Sampling

Available techniques and equipment are presented, with an emphasis on safety techniques and the proper packaging, labeling, and shipping of samples.

QA/QC/Legal Considerations

WESTON considers proper QA/QC to be paramount in terms of safe and effective response operations. Therefore, personnel are made aware of corporate QA/QC SOPs, and the legal and moral implications of properly executing field procedures.

Field Simulation

A three to four hour integrated exercise in which students practice the concepts mentioned in the lectures is conducted. A Team Leader, a Safety Officer, an Equipment Officer, and Work Party Members are designated and tasks and goals are assigned to the team. These may include sampling a series of drums, or collecting air samples, for example. All necessary background information and equipment is supplied. Students operate as much of the available equipment as possible, and set up decontamination and site control zones, etc. A critique is held after the simulation in which team members present their unique approach to the assigned tasks.

Training Manual

As an adjunct to the training course, personnel are provided with a 600 page manual which details all aspects of health and safety for hazardous materials response operations.

CONCLUSION

WESTON has designed an effective health and safety and training program for response personnel, and has successfully implemented it for field personnel involved with hazardous materials. Corporate commitment, medical surveillance, accident reporting, regular communication and training, and QA/QC have been the keys to the success of this program. By implementing the program, WESTON is assured of meeting its moral and legal obligations to its employees.

HEAT STRESS MONITORING AT UNCONTROLLED HAZARDOUS WASTE SITES

RODNEY D. TURPIN
SAFETY AND OCCUPATIONAL HEALTH MANAGER
U.S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESPONSE TEAM
EDISON, NEW JERSEY

INTRODUCTION

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to Federal On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters/Regional Offices, and other governmental agencies in the area of environmental emergency issues such as chemical spills and uncontrolled hazardous waste sites.

It is not the intent of this paper to deliver EPA policy or discuss the development of such policy. Rather, to share with you some of ERT's experiences in dealing with hot workplace environments at hazardous waste sites and monitoring employees for heat stress. While the U.S. Environmental Protection Agency Office of Emergency and Remedial Response (OERR), Hazardous Response Support Division (HRSO), Interim Standard Operating Safety Guides is not EPA policy, it is used by many EPA personnel as a basic reference in addressing such site specific problems.

OVERVIEW OF INTERIM STANDARD OPERATING SAFETY GUIDES, Sept. 1982

The Interim Standard Operating Safety Guides, Sept. 1982 suggests there are four primary classifications for protective clothing and respirator protection:

- Level A = Encapsulating suit with SCBA
- Level B = Hooded chemical splash suit with SCBA
- Level C = Hooded skin protection with air purifying canister respirator
- Level D = No respirator protection and minimum skin protectors

Since the Guides discourage the use of Level D on-site, site activities are conducted in Level A, B, or C and present potential problems for heat stress during warmer periods. In addition, many of the EPA Regions find themselves with the additional problem of working in areas where temperatures and humidity are higher than generally found within the continental United States.

The Guides suggest a heat stress monitoring program be implemented when employees are wearing impervious clothing and ambient temperatures are 70°F or above. The frequency of monitoring should increase as the temperature increases and employees should be monitored after every work period once the temperature exceeds 85° F. The Guides suggest the following monitoring program:

1. Heart rate (HR) should be measured by the radial pulse for 30 seconds as early as possible in the resting period. The HR at the beginning of the rest period should not exceed 110 beats per minute. If the HR is higher the next work period should be shortened by 10 minutes (or 33%), while the length of the rest

period stays the same. If the pulse rate is 100 beats per minute at the beginning of the next rest period, the following work cycle should be shortened by 33%.

2. Body temperature should be measured orally with a clinical thermometer as early as possible in the resting period. Oral temperature (OT) at the beginning of the rest period should not exceed 99°F. If it does, the next work period should be shortened by 10 minutes (or 33%), while the length of the rest period stays the same. However, if the OT exceeds 99.7°F at the beginning of the next period the following work cycle should be further shortened by 33%. OT should be measured again at the end of the rest period to make sure that it has dropped below 99°F.
3. Body water loss (BWL) due to sweating should be measured by weighing the worker in the morning and in the evening. The clothing worn should be similar at both weighings, preferably the worker should be nude. The scale should be accurate to plus or minus 1/4 lb. BWL should not exceed 1.5% of the total body weight. If it does, the worker should be instructed to increase his daily intake of fluids by the weight lost. Ideally, body fluids should be maintained at a constant level during the work day. This requires replacement of electrolytes lost through sweating as well.
4. Good hygienic standards must be maintained by frequent change of clothing and daily showering. Clothing should be permitted to dry during rest periods. Persons who notice skin problems should immediately consult medical personnel.

While these guidelines are extremely helpful, implementation is not always possible at every hazardous waste site. For example, the Environmental Response Team, as well as various EPA Regional personnel have found it extremely difficult to obtain body weights on-site. ERT has found it helpful to obtain worker blood pressures as a substitute for body weighing. While this is not a direct measurement for heat stress, it does alert on-site safety and health professionals to keep close watch on those employees showing potential signs of overall stress as the response develops.

Case History - Dioxin Site, New Jersey

Of interest, is the equipment implemented for heat stress monitoring during the work activity on hot, humid summer days in New Jersey. The site, consisting of a few acres, was located within an industrial park in central New Jersey. It consisted of several large concrete slabs which were once warehouses floors, deteriorated asphalt parking lots, storm drains, sand/clay/gravel areas or outcroppings, and some vegetation areas.

All site personnel were wearing Level C protection consisting of disposable saran coated Tyvek suits with hoods, full face air purifying respirator with industrial size pesticide canisters, gloves, etc. The on-site tasks consisted of two major efforts: collecting and blending soil samples.

The blending operation required the use of 110 A/C current and was located near the decontamination area. Since shade trees were absent, inexpensive beach umbrellas were purchased and placed within the area to extend the work periods from the scheduled 20 minutes. Blender personnel

were in the same Level C protection as the samplers, however, they did not have communication radios.

The soil samplers were in Level C protective equipment and worked for 20 minutes with a 20 minute break. The sample grid had been laid out in advance to reduce the amount of time on-site. This decon line was modified slightly from those set forth in the Interim Standard Operating Safety Guides by adding an annex. This annex was the designated rest area located just past the gross decon area in the decon line. This area was shady and stools were provided for the rest periods.

In attempting to implement heat stress monitoring as described in the Guides, the following were some of the major problems encountered:

1. The accuracy of the weight scale was inconsistent.
2. The blood pressures were hard to hear and a limited number of people were qualified to take them.
3. The decon line was slowed due to the timely process of taking temperatures.
4. It was difficult for the site Health and Safety Officer to take pulses at the appropriate time.

The following is a summary of how the problems were addressed and resolved:

1. Since the duration of the on-site sampling project was less than 6 days the body weight requirement was deleted from the on-site monitoring. Blood pressure measurements were taken, rather than body weight, at each rest period.

2. Initially, the blood pressure was obtained with a traditional stethoscope and sphygmomanometer. However, two major drawbacks occurred:
 - a. The on-site Safety and Health personnel had a difficult time hearing pulse during blood pressure measurement due to background noises, i.e., diesel engines and employee conversations.
 - b. In addition, it took approximately 3 to 8 minutes to monitor each person coming into the rest area. This type of monitoring became a "bottle neck" in personnel traffic flow. The problems were eliminated by incorporating the use of three digital electronic blood pressure monitors.
3. Oral temperatures were originally collected using a traditional oral thermometer and this had an adverse effect on personnel movement through the decon line. This problem was eliminated by the use of several digital thermometers for the sampling crew to use during their rest period.
4. Pulse rates were taken at the wrist or throat. This was time consuming and a difficult task to conduct on personnel coming off the site. This problem was solved since the digital electronic blood pressure monitors also took pulse rates.

CONCLUSION:

As hazardous waste site occupational health and safety professionals know heat stress monitoring is only one of many difficult problems present during most operations. In addition to site conditions, one must consider other factors such as overweight workers, smokers vs. non-smokers, and the

food consumption of the employees during off-duty time. Also, the wearing of dark plastic or rubberized items being heated by the sun can cause increased potential for burns.

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CONSIDERATIONS FOR THE DEVELOPMENT OF A
HAZARDOUS CHEMICAL PERSONNEL PROTECTION SYSTEM*

Jeffrey O. Stull
U.S. Coast Guard
Office of Research and Development
2100 2nd Street SW
Washington, DC 20953

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- * The opinions or assertions contained herein are the private ones of the author and are not to be construed as official or reflecting the views of the Commandant or the Coast Guard at large.

CONSIDERATIONS FOR DEVELOPING A
COMPREHENSIVE HAZARDOUS CHEMICAL PERSONNEL PROTECTION PROGRAM

Unlike chemical industry, those in public hazardous chemical response cannot always predict which chemicals they are likely to encounter. Nonetheless, these are the same people who must be prepared to monitor and mitigate actual or potential releases for any number and combination of hazardous chemicals. Contingent on their capabilities is an adequate form of personnel protection. Yet, because of the wide range of chemicals that can be encountered in spills, derailments, and at chemical waste dumps with the associated variety of potential hazards presented by these chemicals, the selection of chemical protective clothing involves a multiplicity of problems. In some cases, the information to make a selection is available but not consolidated for easy reference. Often, there is a lack of information for the "best" choice, or the existing information is incorrect. But more dangerously there are serious misconceptions as to the proper employment and limitations of chemical protective clothing. These shortcomings for adequate personnel protection can be overcome with a comprehensive program which examines all levels of protective clothing to both identify and implement needed improvements in deficient areas. The U.S. Coast Guard with the help of other governmental organizations is attempting such a program.

Defining the Problem

Classifying the nature of the hazard and the required levels of protection has allowed the Coast Guard and other agencies to devise manageable approaches to optimize personnel protection clothing systems. Of the chemical hazards listed below,

- a) flammability,
- b) reactivity (explosiveness),
- c) corrosion,
- d) toxicity, and
- e) oxygen deficiency,

chemical protective clothing is designed primarily for protection against corrosion and toxicity; Together with a self-contained breathing apparatus (SCBA), the personnel protection system further protects against oxygen deficiency. Fire and explosion hazards must be dealt with separately since current technology does not allow either a practical or economic merger of fire/explosion and chemical toxicity protection. Within the chemical toxicity and corrosion hazards, there are four accepted levels of personnel protection defined by the the U.S. Environmental Protection Agency (EPA) ranging from a totally encapsulated suit with SCBA to cotton overalls (see Table 1). Surveying existing commercial clothing and accessories at each of these level reveals that adequate personnel protection is provided by many items in Classes B and C, but questionable protection is offered by encapsulated suits for category A protection. Whereas guidelines can be established to wisely select Class B and C chemical protective clothing, extensive research, development, and testing is needed in conjunction with performance standards to provide greater confidence for the highest level of protection, Level A protective clothing.

Any research and development program to improve Level A protective clothing must examine both design improvements and extensive suit materials testing. Level A protective clothing includes totally encapsulating suits that have the objective of completely protecting the user against any form of chemical exposure — via respiration, skin absorption, and ingestion. Generally commercial suits have the same salient features, but they are not consistently incorporated in all available versions. The design of these suits involve much more than simple tailoring; specific engineering is needed for the suit to maintain a leak-free, positive pressure atmosphere. Important design features include the construction of seams, the type and location of the zipper, and the suit exhaust valve. The suit must also integrate with either one or several types of breathing systems. Of fundamental importance are the materials of construction which provide the physical strength for the suits and protect against various hazardous chemicals. Each material used in an encapsulated suit must be assessed for its physical properties and chemical resistance. Particularly significant are the selection of test methods and the chemicals used to 'challenge' the suit material. This task is especially difficult when an organization must consider an unknown number of hazardous chemicals.

Although any large list of chemicals remains diverse, it is still necessary to rank hazardous chemicals in priority order to achieve a workable approach to develop a personnel protection system. In 1974, the Coast Guard established the Chemical Hazard Response Information System (CHRIS) now listing over 1000 chemical which might be discharged into inland or coastal waterways (CHRIS provides a complete description of the chemical and recommends appropriate response techniques for each listed chemical [1]). Over 40% of these CHRIS chemicals were found to require use of an encapsulated or sealed suit based on toxicological data [2] (Sax's Toxic Hazard Ratings [3]). Still, not all these chemicals are likely to be encountered in hazardous chemical response on a routine basis. Table 2 shows the top 25 chemicals based on spill frequency to which the Coast Guard responded to between 1974 and 1983. Yet, developing a personnel protection system for only those chemicals seen in the field incurs potential risk since there will always be spills of chemicals which cannot be anticipated. For example, over the same period that the information in Table 2 was accumulated, 53 identified substances were involved in Coast Guard hazardous response only once. This does not justify development of the personnel protection system for every chemical encountered, but it does mean that any system developed must be flexible enough to accommodate a variety of spilled substances. As a result of these difficulties, the Coast Guard has adopted a priority list of compounds which not only takes into account commonly spilled chemicals, but also the amounts of chemicals transported (i.e., the likelihood of their being spilled), the forms in which they are transported, and the potential toxicity and dermal effects of these chemicals. Beginning with a priority chemical list, chemical compatibility information can be generated to cover the majority of expected situations; other chemicals can be added to the system once established to extend the system to additional situations.

Suit Material Compatibility

Probably the most important characteristic used in selecting or developing chemical protective clothing is the choice of materials. The major premise behind chemical protective clothing is that it acts as an 'impervious' barrier to hazardous chemicals. Though much of this depends on how well the suit is constructed, the ability of the suit material(s) to resist chemical intrusion or 'breakthrough' is paramount. In the past few years, especially with the formation of the American Society of Testing and Materials (ASTM) F23 Committee on "Chemical Protective Clothing" in 1977, numerous studies have revealed that a number of assumptions on the chemical protection offered by existing clothing do not hold true. With the advent of a new ASTM procedures for determining chemical resistance of materials, more limitations are being discovered which necessitate new approaches to designing, testing, and using chemical protective clothing.

Types of Chemical Intrusion. When a suit material resists intrusion by a hazardous chemical, the material is said to be 'compatible' with that chemical. The ASTM F23 Committee has defined three processes by which a chemical can affect a suit material and/or gain access into a suit or other forms of protective clothing:

1. Degradation - The deterioration in the material of one or more physical properties upon surface contact by a chemical. For example, a change in material weight through surface contact of a chemical could be such an indicator.
2. Penetration - The flow of a liquid or gaseous chemical on a non-molecular level through closures, porous materials, seams, pinholes, or other imperfections in a protective clothing material.
3. Permeation - The process by which a liquid or gaseous chemical moves through a protective clothing material on a molecular level via:
 - a. adsorption of the chemical onto the surface of the material,
 - b. diffusion into the material, and
 - c. desorption of the chemical from the inner surface of the material.

Each phenomena raises different concerns about the viability of a protective clothing material. Degradation is usually a detectable change of the material which can be observed visually or instrumentally. Visual changes to the material may be readily apparent such as swelling, discoloration, delamination (of composite materials), and shrinking. Two commonly used measures for determining degradation, in addition to visually observed effects, include weight change and elongation. Other changes may not be as easily measured or noticed following a chemical

exposure such as tensile strength and abrasion resistance. Yet, changes in these material physical properties can also adversely affect the integrity of protective clothing.

The extent of penetration for a piece of protective clothing or its components (zipper, visor, etc.) can be a measure of how well that item is put together. It is also an indicator of the material quality itself, particularly for coated fabrics. The process of laminating composite materials and coating fabrics can form imperfections in those materials due to improper curing or thin application of the polymer film; this can result in material pinholes and inconsistent layer thickness providing an avenue for chemical penetration. However, chemical penetration is most likely to occur at seams, through the zipper, or around the exhaust valve of Level A protective clothing. This phenomena can be influenced by a number of conditions including design, wear, and temperature.

Permeation is the most insidious of the processes since a perfectly intact suit showing no visible adverse effects to a chemical can undergo permeation without the knowledge of the user. Furthermore, it is only after the material has accumulated within the suit at a detectable concentration, that it is first noticed by the user (if the chemical is detected by human senses). The time it takes for a chemical to initially adsorb, diffuse, and then desorb, and be detected on the other side of the material, is called the 'breakthrough' time. The breakthrough time together with the rate of permeation are used to characterize the permeation resistance of a material. In some cases, once breakthrough is achieved, the chemical may permeate at a constant rate for 'steady-state' permeation. In other cases, permeation may continue to increase at a slow rate. Nevertheless, the breakthrough time is the most commonly used measure to establish chemical compatibility. It is important to note that permeation may occur without degradation and the opposing case is also possible.

Limitations of Current Compatibility Information. Both degradation and permeation data are used to establish material-chemical compatibility recommendations. Compatibility recommendations are an interpretation of the chemical resistance data based on exposure criteria. The exposure criteria is set by the particular application. For Level A suits, the material might have to successfully resist chemical attack or permeation for one to three hours; glove users often use an eight hour criteria. The criteria must be carefully established, particularly in multi-chemical response, because there is no one suit material that has been tested that will resist degradation or permeation by all chemicals, much less by a majority of the common hazardous chemicals. For level A protection, this means that multi-chemical response teams must carry an inventory of two or more encapsulated suits constructed of different protective materials. The Coast Guard has selected three -- viton, butyl rubber, and chlorinated polyethylene with a fluorinated ethylene propylene visor to provide broad coverage against the hazardous chemicals they expect to encounter [4].

Data covering measurements for the above phenomena in most material-chemical combinations is not available. This is partly because these definitions or methods for their repeatable measurement did not exist until the last few years. As a result, much of the existing

recommendations for using chemical protective clothing lack sufficient basis and must be regarded with caution. Table 3 shows a material-chemical matrix for some representative challenge chemicals and protective clothing materials. Each material in the table demonstrates incompatibility to a number of chemicals. More illustrative of the chemical resistance characteristics of these same materials is a material-chemical class matrix presented in Table 4. Particularly noteworthy are the absence of, and type of data presented in this table. The recommendations in Table 4 were taken from a consolidated source for protective clothing compatibility [5], and are not necessarily supported by actual data (indicated by the lower case designations). This means that the recommendations may not be based on data from standard test methods or they have been inferred by chemical resistance behavior for similar material-chemical pairs. The reliability of such data must remain questionable until proven otherwise.

Serious misconceptions can arise from the way material-chemical data is presented. Material compatibility information is often presented for protective clothing items using simple rating formats less diverse than those appearing in Table 4A; usually a system is employed using ratings of excellent, good, average, and fair with corresponding letters or numbers. In some cases, a recommended time period for the compatibility rating is given, e.g., "resistance time at least four hours; material slightly affected". Even when such information is provided, the method used to make that determination is not always documented. If a complete description of the testing and test results are available to support the recommendation, then some confidence in the recommendation can be assumed for the subject material. Such information is often unavailable for the materials in Level A protective clothing.

What remains a more serious problem is the basis for recommending a Level A encapsulated suit. Whatever recommendation is made for the suit, it is made using the compatibility information of the primary material only. That is, secondary materials such as those used in the visor, boots, gloves, and external suit fittings are not taken into account for recommending overall suit compatibility to a particular chemical. In reality, the integrity of a suit to resist chemical intrusion is only as good as its weakest material. This fact received widespread attention when the polyvinyl chloride (PVC) visors of two commercial butyl rubber encapsulated suits failed when exposed to vapors of anhydrous dimethyl amine. The incident occurred when the fire department in Benecia, California responded to leaking tank railcars containing that substance. The facepieces of each suit "cracked open in a shattering manner" exposing the users to the chemical vapors [6]. Some sources show butyl rubber having limited compatibility with dimethyl amine; compatibility data is not available for PVC. During that incident, leaks also developed in the seams of the suits. Similarly, the adhesive used to bond the seams of a chlorobutyl suit broke down when exposed to muriatic acid during an industrial operation resulting in a serious accident [7]. In each case, the failure of secondary suit materials was partially due to a lack of documentation for their chemical compatibility. These examples demonstrate the need for compatibility information for all external suit materials, with recommendations to use suits based on the least chemically resistant material for each particular chemical.

Another problem in the way chemical compatibility data is presented concerns the documentation of the material and testing procedures. Most material-chemical compatibility tables list ratings for materials like butyl, neoprene, and nitrile rubbers against several chemicals. Yet, these same material names are often 'generic'; material product formulations/processing conditions can vary from manufacturer to manufacturer as well as lot to lot. For example, hundreds of formulations exist for neoprene rubber, a common protective material, each with various fillers and active ingredients that provide slightly different chemical properties [8]. Sometimes the differences can be significant as shown in Table 5 below for the permeation of three butyl rubber formulations by MIBK.

TABLE 5

PERMEATION DATA FOR THREE DIFFERENT BUTYL RUBBER FORMULATIONS [9]

<u>Material/ Formulation</u>	<u>Thickness (mil)</u>	<u>Breakthrough Time (min)</u>		
		<u>DMF</u>	<u>Hexane</u>	<u>MIBK</u>
Butyl rubber A	24-26	No BT	20-25	270-300
Butyl rubber B	24-26	No BT	30	300-340
Butyl Rubber C	23-26	No BT	20	180-200

Other variations in the material, particularly thickness, can affect the reliability of the chemical reliability information. In essence, separate chemical compatibility data must accompany each protective clothing item because there is no certainty on how representative 'generic' data may be.

Methods for Assessing Chemical Resistance.

In the past, both users and manufacturers employed different techniques to report overall compatibility of protective clothing to various chemicals. The inability to compare items with differing supporting data and the fact that some techniques employed did not yield repeatable results led the ASTM F23 Committee to seek development of standardized test methods. ASTM has drafted standard test methods which measure degradation, penetration, and permeation for protective clothing materials. Of these, only the method for measuring permeation (ASTM F739-81) has become an established standard, though revisions to it are now being considered. Possible modifications or supplements to this method include adapting the method for measuring permeation of chemicals in the gaseous phase, intermittent contact by chemicals for 'splash' tests, and more standardization of the method to eliminate the effect of variables that can influence the breakthrough time such as temperature and collection media flowrates.

Degradation. Draft methods for degradation standardize the way in which a material is exposed but allow flexibility for measuring any

physical property to denote a change in the material as the result of the exposure. Most protective clothing manufacturers rely heavily on degradation testing to set up their recommendations in chemical compatibility tables. This is because degradation is a relatively simple and inexpensive test to perform. Essentially a material swatch of known dimensions and weight is exposed to a liquid chemical; observations and measurements are made at set time intervals from the beginning of the exposure. This is basis for the draft ASTM method. Problems arise for some existing data since the exposure was often accomplished by complete immersion of the material swatch, sometimes without sealing the edges of the swatch. The ASTM method ensures one sided exposure of the material to its normal outside surface, which realistically simulates chemical contact with the material. The physical properties commonly chosen for the test are elongation and weight change. Other physical properties can be chosen depending on available equipment and characteristics that are useful to the investigator. For example, one might want to know how tensile strength and flexibility are affected during chemical exposures. However, the greatest utility of the method is for 'screening' materials prior to permeation tests; significant sign of degradation are usually an indication that the material will fail and costly permeation studies are not necessary.

Permeation. Measuring permeation with the ASTM F739-81 method also involves specified procedures for one sided exposure to 'challenge' chemicals. In this case, the apparatus consists of a test cell, a sample pump, and sample analyzer (detector). The test cell (Figure 1) consists of two chambers separated by the material to be tested. One chamber holds the challenge liquid chemical while the other chamber contains the collecting media. The material is mounted between teflon rings and clamped together. The collecting medium can be either gaseous or liquid depending on the nature of the challenge chemical. Following exposure of the material to the challenge chemical, the collected medium is either withdrawn continuously or discretely for analysis. Collection systems can be operated as open or closed. Chemical concentration is plotted versus time in a manner similar to that presented in Figure 2 with subsequent determination of the breakthrough time and steady-state permeation rate. Some variation exists in the method and different results can be obtained from the same technique. Yet, documenting the test method, equipment, and conditions can allow interpretation of this variance. Many ASTM members are in the process of further standardizing this method for more reproducible results.

Variables Affecting Permeation

Permeation is affected by a number of a variables which control accurate and precise measurements of breakthrough time and permeation rate using the ASTM F739-81 method. The equipment used to make the determinations can have a significant impact. For this reason, ASTM designed and adopted a standard test cell for exposing a protective material to a liquid chemical under repeatable conditions. However, other cells have been devised which use less chemical for testing and that are more easily adapted to multiple sample systems [10]. Another

effect of the equipment involves the selection of the detector. Because breakthrough time is directly dependent on the time the chemical is first detected after 'breaking through' the material, it can vary with the sensitivity of the detector. The ASTM method does not specify a detector or type of detector in its procedures; it does require that reported results document the detector used and its sensitivity.

Other variables are related to the fundamental principles governing the permeation process. Many studies have shown that permeation is related to the solubility of the chemical in the clothing material [11,12]. Material-chemical solubility is a function of many factors such as temperature, concentration, and pressure. Table 7 below shows the effect of slight changes in temperature on two protective clothing materials.

Table 7

TEMPERATURE EFFECTS ON BREAKTHROUGH TIME [13]

<u>Test Material</u>	<u>Temp (C)</u>	<u>Acetone BT (min)</u>
Viton/Clorobutyl	20	95-98
	26.5	43-53
30 mil Chlorinated Polyethylene	22	32-35
	24.5	27-31

The type of material, its thickness, and the method used for its manufacture can also affect chemical permeation. Investigation of these variables are warranted because an understanding of the suit material/challenge chemical permeation process may allow prediction of breakthrough time and permeation rate for untested material-chemical pairs. Attempts have been made to model known permeation data on the basis of the challenge chemical's solubility factor, degree of hydrogen bonding, and molecular size showing some correlation [13,14,15]. Several organizations are engaged in such studies including the National Institute for Occupational Safety and Health (NIOSH), the U.S. EPA, and the U.S. Coast Guard.

The primary reason for investigating the effects of variable conditions on protective clothing permeation is to provide data which is more characteristic of actual use. The recommendation to use a particular protective clothing item of a specific material usually rests on the material's breakthrough time to a certain chemical. In nearly all cases, this breakthrough time is measured for 100% pure chemical in contact with the material. This type of material-chemical contact certainly does not represent a realistic exposure for the majority of protective clothing applications (industrial glove and boot use may be an exception). If a material has, for example, a 2 hour breakthrough time for a particular chemical, then one could expect the material to fail after two hours of constant direct exposure with that chemical. This sort of testing is considered to be the 'worst case'. One could assume a large safety factor for using protective clothing in situations with less

than 100% chemical exposure, but tests are still needed to approximate more realistic field conditions to determine the magnitude of safety factors that exist, and assist in establishing criteria for the interpretation of permeation data.

Currently under consideration by ASTM are modifications to the permeation resistance test method (ASTM F739-81) which allow testing using challenge chemicals as gases or vapors, and for reproducible intermittent contact by liquid chemicals. Since the present form of the ASTM method is written for only liquid contact, no standard exists for measuring the permeation of protective materials by permanent gases or chemical vapors. Chemicals in the gaseous state are often encountered in the field. Depending on the temperature and the vapor pressure of normal liquid chemicals, the ambient concentration of a chemical in the air can vary greatly. Of equal concern is intermittent exposure of a protective material to a liquid chemical representing the effect of a 'splash'. Adaptation of the ASTM method is being pursued in both areas. Preliminary experiments using the proposed modified methods were conducted by the Coast Guard Research and Development Center. Generally, vapor and 'splash' testing showed the expected results -- pure liquid breaks through faster than saturated vapors at ambient or reduced temperatures; breakthrough also occurs sooner for pure liquid than for multiple splashes, which breakthrough faster than single splashes [13]. In some instances, however, breakthrough time did not vary significantly with challenge chemical contact time, suggesting wettability of the protective material as an important factor. These results are shown in Figure 3.

Permeation by Chemical Mixtures.

While little information is available for most material-chemical pair permeation, even less information exists for chemical mixtures permeation through protective clothing materials. There is a high probability that mixtures will be encountered in chemical spill or monitoring situations, as they already are. For a chemical mixture spill, there is little basis to assume that the material-chemical compatibility data/recommendations for each chemical can be applied separately to predict the overall effects of the mixture. For example, if one chemical breaks through a material in 15 minutes and another chemical permeates through the same material in 1 hour, then a mixture of the two chemicals or even the most permeable chemical in such a mixture may not break through in 15 minutes. Research of the Coast Guard and other organizations has shown that some mixtures act predictably while others do not. Data in Table 7, provided by the Coast Guard Research and Development Center, indicate gross synergistic effects for hexane/acetone mixtures but 'additive' permeation behavior for methylene chloride in hexane and toluene against viton/chlorobutyl laminate [13]. One of the serious problems posed by mixtures is the selection of chemical protective clothing. As illustrated above, even when the protective material provide protection against all chemicals in the mixture, there is no guarantee that the components acting together will not permeate the material. Furthermore, since chemical compatibility varies with

material, mixtures may be encountered which contain chemicals compatible with some components but not with others. Clearly methods are needed to assess chemical mixture permeation.

Materials Testing Program

The U.S. Coast Guard has discovered many of the problems associated with material-chemical compatibility in the course of its efforts to develop new Level A protective clothing. For a three hour exposure criteria (i.e., no chemical breakthrough in 3 hours), initial materials testing using the ASTM permeation resistance method have shown the Coast Guard selected materials (viton, butyl rubber, and chlorinated polyethylene) to be incompatible with a number of commonly encountered hazardous chemicals (see Table 8). As a consequence, a rigorous and detailed test plan has been developed by the Coast Guard Research and Development Center to thoroughly investigate the permeation process for these materials. The test plan addresses work on new procedures, the effect of several variables, and routine testing of priority chemicals that will provide realistic criteria for suit selection. The end result of this effort will be a 'manual of practice' to accompany deployed suits that informs Coast Guard responders as to the effectiveness and limitations for the protective clothing being used. The 'manual of practice' will be specific to the design and type of suits employed and will be updated to cover more situations and chemicals as materials testing continues.

Though laboratory materials testing can take into account many variables and establish 'reasonable' criteria for protective clothing selection, supplementary approaches are needed to handle situations for which no data exist. One alternative involves determining material-chemical compatibility at the site for unknown chemicals or mixtures. Due to the overwhelming number of possible mixtures in hazardous chemical response, techniques for on-site permeation assessment may provide immediate protective clothing compatibility information. Portable 'field-test' permeation kits are under development by both the U.S. EPA and NIOSH [8] for such purposes, and can also fill a gap for unavailable material-chemical pair data as encountered under actual conditions. As this sort of 'field' data is accumulated, material-chemical compatibility tables and assessment methods can be revised to allow more judicious protective clothing selection.

Decontamination

Once a suit is exposed to a hazardous chemical, there is no simple way to determine the extent of its contamination, and if decontaminated, the effectiveness of the decontamination process. Herein lies the problem of protective clothing decontamination. Further complicating the issue is the fact that once a protective clothing item is exposed to a chemical, it may be permeated to some extent with residual chemical remaining inside but not breaking through the material for the duration of the exposure (material 'matrix' contamination). However, following

the exposure, the chemical may continue to permeate through the material while the item is in storage [16]. Subsequent exposure to the same chemical or a different chemical may drive the original residual chemical through the material, or have synergistic effects if the second exposure involves a different chemical. In essence, potential risk is assumed for reusing protective clothing that has been exposed to a hazardous chemical.

Any alternative to suit or clothing disposal following chemical exposure, i.e., decontamination, depends on the development of methods to determine the level of contamination for an exposed article. Additionally, the phenomena of material 'matrix' contamination must be verified and its significance determined. Because different decontamination processes may be involved, there must be an ability to distinguish between surface and 'matrix' contamination. The Coast Guard intends to investigate this problem through two approaches. The first approach involves an in-depth analysis of materials exposed to chemicals with different contact times less than the established breakthrough time for the chosen material-chemical pair. Radioactive tracer chemicals will be employed to determine a concentration 'profile' of the chemical in a cross section of the material, if any. This will show the extent of permeation and will help define the problem for evaluating decontamination methods. The second method addresses a survey of physical property methods to determine gross amounts of residual chemical within the material, and any changes occurring to the material as the result of the exposure. So far, thermal analysis techniques such as differential scanning calorimetry and thermogravimetric analysis show the greatest promise for this application [17]. These methods may be easily applied to assess protective clothing contamination before and after a decontamination process, with the information used to determine the viability of reusing the clothing item.

Once protective clothing contamination can be measured accurately, decontamination methods may be found that can completely remove that contamination. Several methods are being employed which have potential for protective clothing decontamination. Water and certain detergents appear effective against many inorganic and some organic contaminants. A Freon-based 'washing machine' or shower system (for encapsulated suits) shows promise for removing many organic substances [18]. However, if the above studies yield results showing significant 'matrix' contamination for most exposures, then development of decontamination methods will be difficult for cleaning protective materials without affecting the chemical resistance or physical properties of the material. Development of new materials may be considered which are more 'inert' and are only surface contaminated. Such materials in combination with effective decontamination methods may offer an economic alternative to disposal of protective suit and clothing constructed of relatively cheaper materials.

Physical Properties of Protective Materials

In addition to chemical resistance, the physical properties of a protective clothing material are also important in selecting the appropriate material for a particular application. The majority of materials used in protective clothing today have been around for the past

decade, but many variations of each material exist, each with different physical properties. Protective clothing materials may be fabrics, thick polymer films, or coated fabrics. Some coated fabrics can be quite complex — a different coating may exist on either side of the fabric, more than one substrate can be used in a material, or films may be layered together to form composite materials. As polymer films vary (butyl rubber, neoprene, PVC, and viton), so do substrates (nylon, polyester, nomen) which are both woven or non-woven. Level A protective clothing generally involves fabrics coated with polymer films. These types of materials combine the chemical resistance characteristics of the polymer with the physical support of cloth.

Some physical properties are characteristic of the entire material while others are attributed to either the coating or the substrate cloth. Physical properties that apply to the entire material include material thickness, typically measured in 'mils' (thousandths of an inch), and weight, most often reported in ounces per square yard. The strength of a material (tensile, tearing, and bursting) and its ability to resist physical abuse (abrasion and punctures) is mostly a function of the substrate. Material flexibility and brittleness is often associated with the polymer film, though sometimes the overall material can influence these properties. Flammability, a characteristic included in the list of physical properties is highly dependent on the polymer coating (NOTE: Favorable flammability properties of a material should not be used to infer any fire protective qualities for a particular item of protective clothing). A List of physical properties and established test methods which can be used for their measurement are given in Table 9.

The requirements for these physical properties depend on the application of protective clothing employing the selected material. Weight and thickness are usually best kept at a minimum but tradeoffs are involved that pose advantages and disadvantages for other physical properties. Using a low weight and thin material might offer better comfort to the wearer in terms of flexibility and bending, but physical strength and resistance might be sacrificed (along with chemical resistance). Such lightweight materials are used in disposal commercial tyvek or saranex type suits. Most multichemical response organizations use encapsulated suits made from materials that are relatively heavy and possess high strength characteristics for multiple use in either training or actual responses. Typical requirements for this application are given in Table 9.

Encapsulated Suit Design Problems

The basic configuration of an encapsulated suit varies from one manufacturer to another. An example of an encapsulated suit is sketched in Figure 4. Generally fully encapsulated suits have the same components — a full body garment with gloves, boots, visor, exhaust system, entry location (e.g. zipper), space for a breathing system or an interface for one, and sometimes a cooling system. Most radical differences between suits involve the type of breathing system and how it interfaces with the suit, but several other differences can exist. This diversity of suit design offers different design features to accommodate the needs of

multi-chemical response teams. In some cases, variation in suit design is useful as called for by the particular application or operations of the user organization.

Suit variation is often distributed between tailoring changes which do not affect the operation of the suit, and fundamental changes which can have a significant impact on the way a suit operates. Tailoring differences between suits typically deal with suit sizing and the space provided inside a suit for the variety of breathing systems and headgear (hardhats and communications). Another example of this design feature type would include whether the boots and gloves are permanently attached and the location of the zipper. These latter issues are not lightly considered and could be conceivably placed in the other category. Many multichemical response organizations, i.e., local fire department hazardous chemical teams disagree whether the zipper should be accessible to the suit user or not [19] (the zipper is commercially found either in the back or on the side). On the other hand, fundamental design changes might encompass the type of zipper, its sealing mechanism, and the way the zipper is designed. Additional features such as the type and number of suit exhaust valves, the visor/hood configuration, and provisions for cooling and breathing system interfaces all affect suit operation and differ in available commercial suits.

Certain design standards should be universal to all Level A protective clothing. Extremely important are the design of seams, the zipper, and other items in which different materials interface (visor, gloves, boots, zipper, etc) or where an opening exists (e.g., exhaust valves, inflation valve, and zipper). These features all contribute to overall suit integrity for maintaining positive pressure operation; a deficiency in any item can seriously impair the protective capability of the suit as much as a chemically permeable material. The nature of designing such items is highly dependent on the materials used in fabricating the suit. Generally, there are two types of materials which dictate two different fabrication procedures. Some materials like chlorinated polyethylene (CPE) and polyvinyl chloride are heat-sealable and are joined in seams dielectrically. Otherwise, materials such as butyl rubber, nitrile rubber, and viton must be sewn together and then patched with a strip of material bonded over the seam with an adhesive. Modified or combined techniques exist for the many materials used in encapsulated suits, some specific for the material employed. Since there are a variety of suit construction methods each having its merits, standards must primarily apply to the performance of the suit and its components and less in the form of individual item design specifications.

The basis for many suit and suit component performance specifications now exist in the form of established or draft federal, military, and consensus organization standards including those of ASTM, the American National Standards Institute (ANSI), and the National Fire Protection Association (NFPA). For example, test methods are available to determine seam strength (ASTM D751-79) and establish quality control practices for sewing coated fabric seams (U.S. Federal Standard 751). The draft ASTM test method for measuring chemical penetration will be useful to assess seams, zippers, visors, and other material interfaces that affect suit integrity. Other standard techniques under development address total suit (ensemble) performance. One such method allows users

to simply determine gross suit leakage by inflating the suit to a specified pressure and covering seams with a soap film. More standards will be necessary to address manufacturer quality assurance. But more importantly, it will be necessary to organize the individual standards and test methods in a comprehensive performance specification for encapsulated suits in multi-chemical response. This kind of an overall standard can establish minimum requirements for Level A protective clothing, for which none currently exist. This would be especially useful to the smaller organizations that do not possess the resources to verify the quality of commercial chemical protective clothing.

Chemical Clothing Selection Guidelines

While a comprehensive specification for Level A encapsulated suits guarantees some minimum performance for such protective clothing, similar standards for Level B and C clothing might prove impractical due to the diversity of clothing and clothing types, even in the application of multi-chemical response. An alternative is the development of an information base and criteria which will allow users to select protective clothing such as non-encapsulated suits, gloves, aprons, and boots wisely for their own specific needs. In 1983, the American Conference of Government Industrial Hygienists (ACGIH) published, "Guidelines for the Selection of Chemical Protective Clothing" consolidating chemical compatibility data and manufacturer information on protective clothing items [5]. This work was sponsored by the U.S. EPA to allow chemical industry and response organizations to optimize their procurement of chemical protective clothing. The reference allows a user to select the 'appropriate' protective material for a specific chemical, and then selecting the clothing item needed (glove, suit, etc.), find out what manufacturers make the item in the recommended material. Shortcomings of the recommendations are explained and a full background on chemical protective clothing is given. This reference currently represents the largest public collection of chemical protective clothing information.

The U.S. Coast Guard intends to supplement EPA's "Guidelines..." with additional information to further promote its utility to assist a protective clothing user to make wise decisions in procuring and using chemical protective clothing. In many cases, actual material-chemical compatibility data for particular materials is necessary in lieu of recommendations to determine protective clothing applications not meeting the one hour criteria used in the "Guidelines...". One objective of the Coast Guard program will be to provide this data in an appendix or other form within the ACGIH reference. Another need exists for listing material physical properties for 'specified' common protective clothing materials. This will allow the user to characterize the materials for physical properties necessary to the particular application. Further, providing documentation to compare chemical clothing design features will assist organizations in making procurement decisions without relying on manufacturers' literature. To supplement this information, the Coast Guard plans on providing information on general quality assurance

practices. A new edition of the "Guidelines for the Selection of Chemical Protective Clothing" would contain:

1. A material-chemical compatibility index,
2. A list of material physical properties,
3. A list of items made in each material for all manufacturers,
4. A design feature - manufacturer item matrix,
5. Quality assurance practices that are or should be used by manufacturers.
6. A vendor's directory
7. Background information on chemical protective clothing and permeation theory as provided in the first edition.

The U.S. EPA, NIOSH, and the Coast Guard are seeking to devise a database for the above information for continual updating.

Summary

In the effort to provide adequate personnel protection during hazardous chemical and response, the U. S. Coast Guard and other multi-chemical response organizations have discovered many limitations of chemical protective clothing in terms of design, material-chemical compatibility, and decontamination. These deficiencies have led to the establishment of a comprehensive hazardous chemical personnel protection program. This program entails two approaches -- 1) Set up informative guidelines for the wise selection of Level B and C protective clothing; and 2) Develop improved Level A protective clothing through improvements in design and extensive materials testing. Concurrent with these efforts is strong participation in the ASTM F23 Committee on Chemical Protective Clothing to establish standards which set requirements for protective clothing performance and testing. In the federal government, we have the unique position of making substantial advances in each area. We possess the resources to design equipment and clothing that meet chemical protection needs, we can perform the necessary background R&D to support those designs, and we can advocate our specifications to form the basis of standards for general industry to encourage minimum standards of personnel protection.

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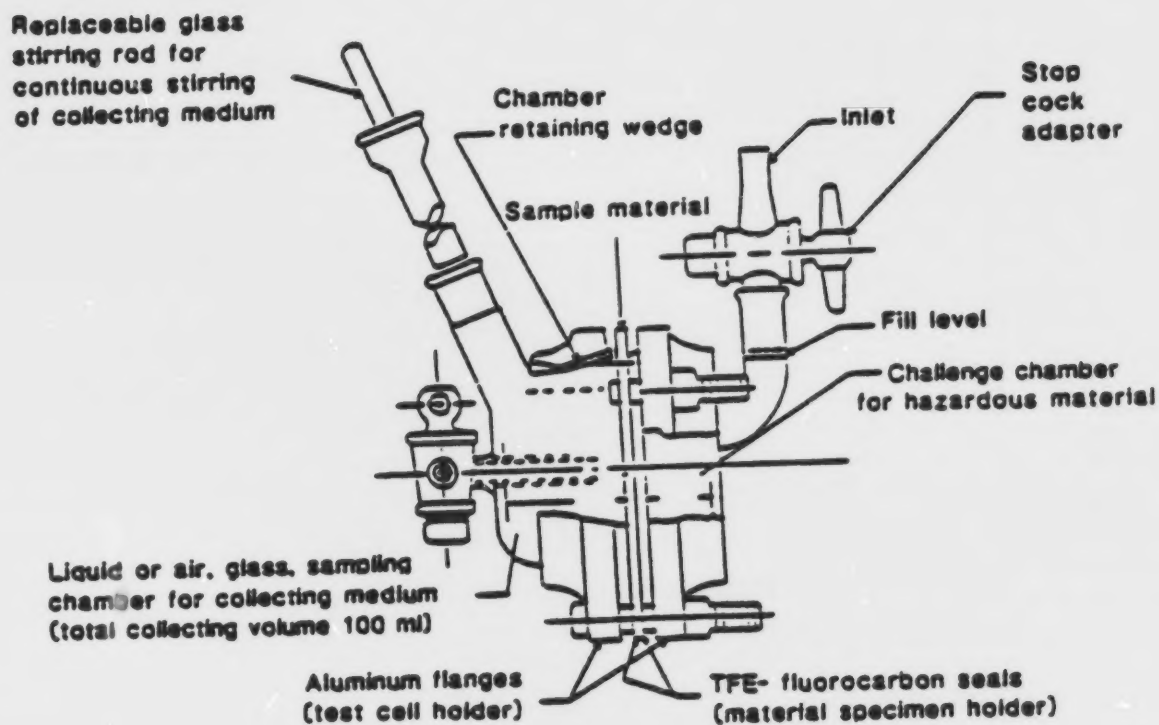


Figure 1. Chemical Permeation Test Cell

(ASTM Standard Test Method F739-81)

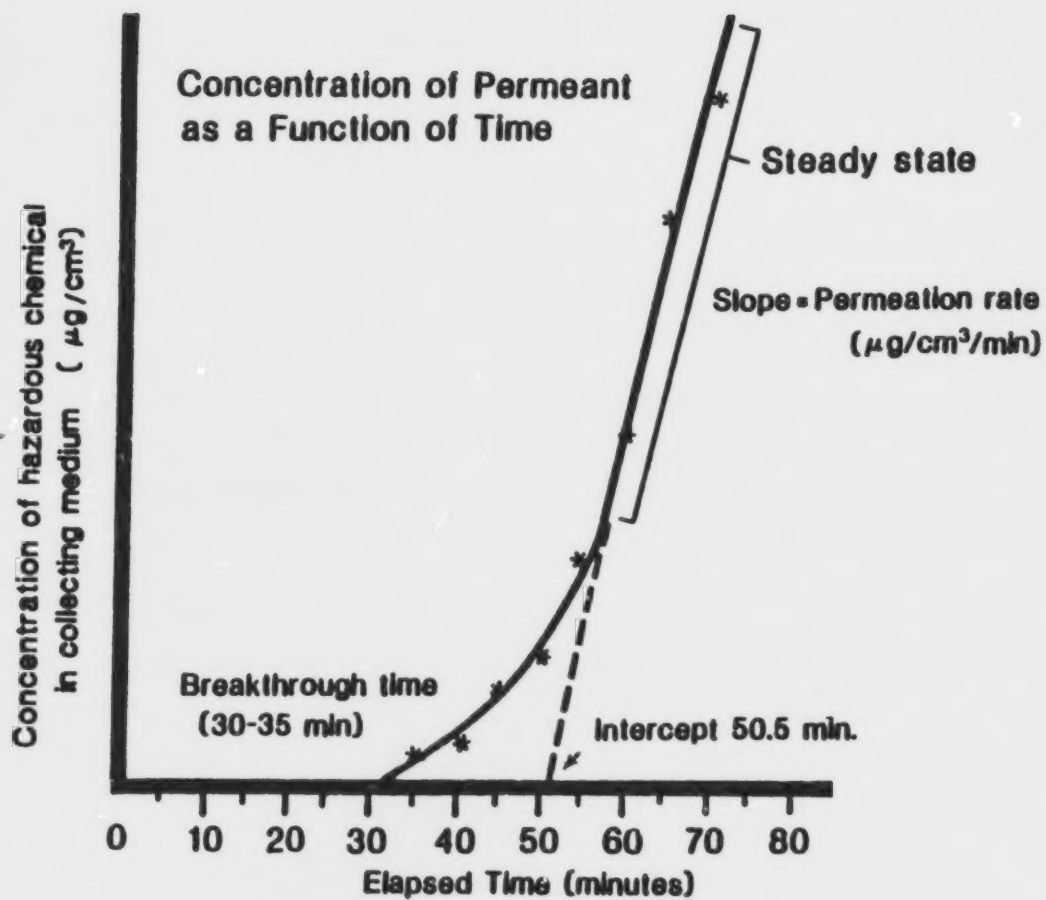
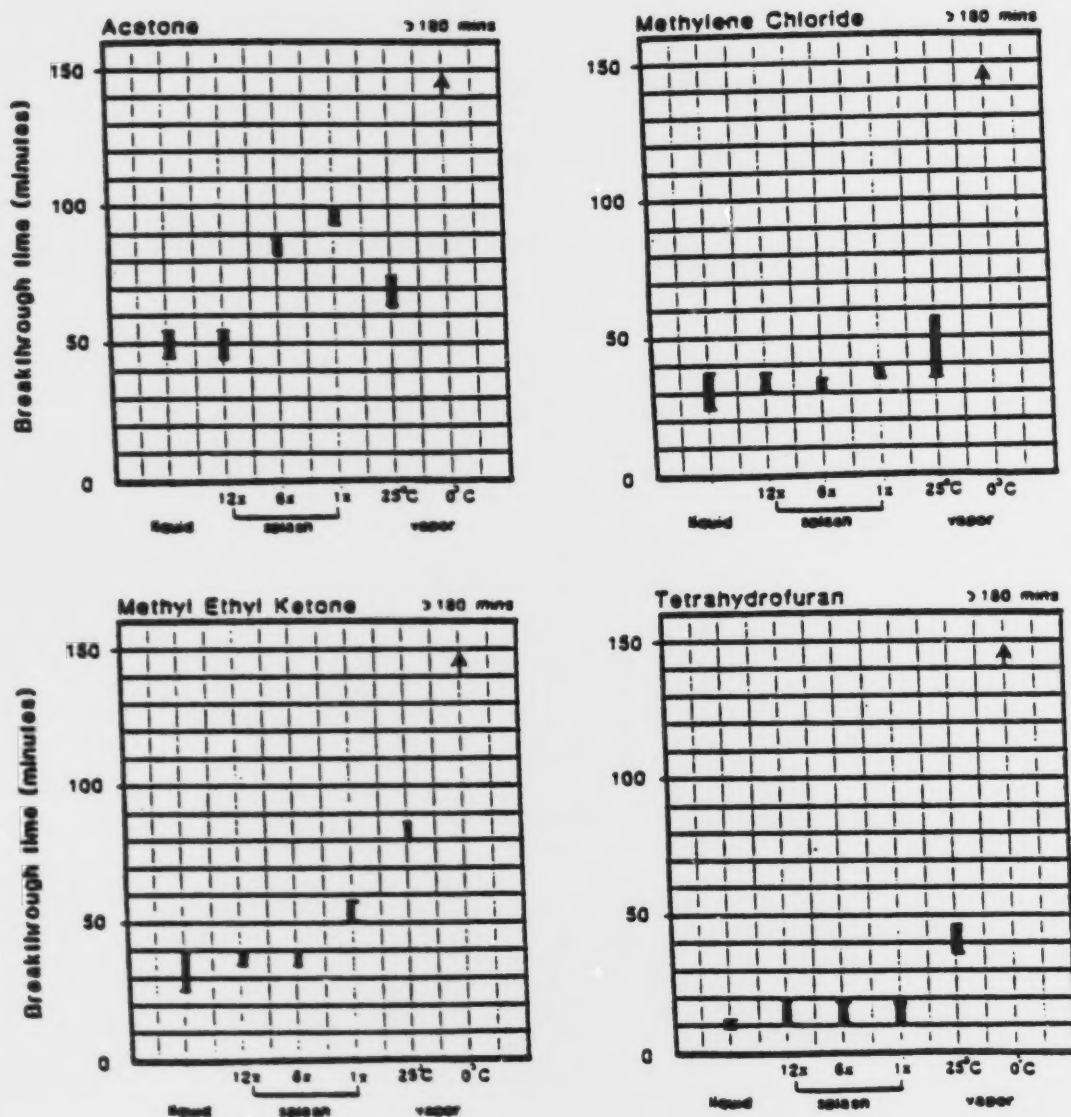


Figure 2. Graphical Method to Determine Breakthrough Time and Steady-State Permeation Rate



KEY: liquid - Breakthrough time determined using ASTM F739-81
 splash 12x - 12 'splashes' at 15 minute intervals over 3 hour period
 6x - 6 'splashes' at 30 minute intervals over 3 hour period
 1x - one 'splash' at beginning of test
 vapor - saturated vapor at 0°C or 25°C in contact with material

Figure 3. Liquid, 'Splash', and Vapor Permeation Tests for Representative Hazardous Chemicals

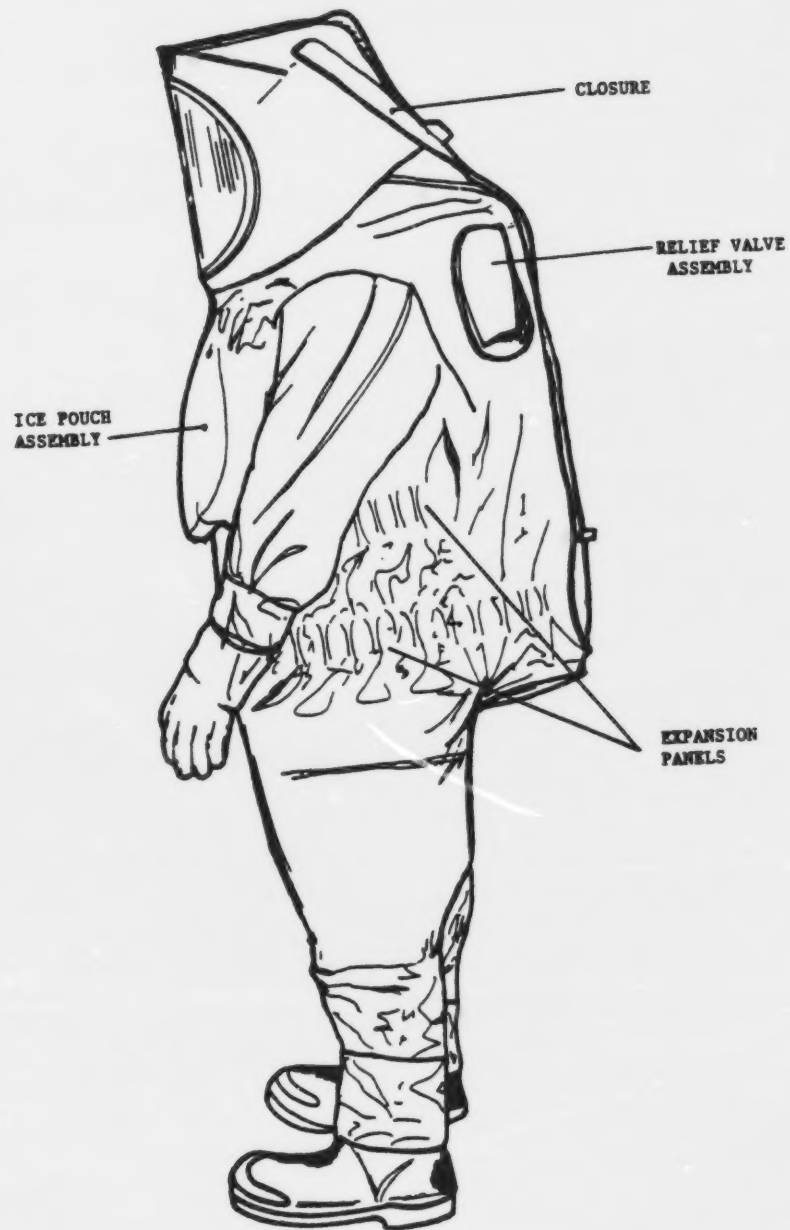


Figure 4. Coast Guard Encapsulated Suit Design

TABLE 1
PROTECTIVE CLOTHING CATEGORIES

- LEVEL A - protective clothing that is used when the threat is the greatest, and no contact may be permitted. The level incorporates a totally encapsulated suit to prevent skin contact of any kind and a self-contained breathing apparatus (SCBA) inside, for two separate seals between the outside air and the user's respiratory system (Type I). Two variations of this level involve only one seal, with the SCBA worn on the outside (Type II), and using an airline breathing system (Type III).
- LEVEL B - protective clothing that is used in cases where limited skin contact with vapors may be acceptable. The garment covers most of the body, but not completely, and it is not completely sealed, so there is a possibility of the chemical making contact with the skin. The respiratory equipment is an SCBA.
- LEVEL C - protective clothing resembling Level B, but the respiratory protection is not critical and an air-purifying purifier (a filter-type "gas mask") replaces the SCBA. The garments for Levels B and C do not protect against vapors, but only against liquids that may splash on the individual. Levels B and C clothing are generally referred to as a "splash suit"
- LEVEL D - this protective clothing is essentially a pair of coveralls with boots and gloves. Level D protection is used in the limited number of cases when there is not indication of hazardous conditions and the work function precludes contact with hazardous substances.

TABLE 2

TOP 25 CHEMICALS SPILLED FROM 1973 TO 1983
TO WHICH THE COAST GUARD RESPONDED

<u>Rank</u>	<u>Chemical Name</u>	<u>No. of Spills</u>	<u>Reported Gallons</u>	<u>Quantities Pounds</u>	<u>Most Recent</u>	<u>Level A Protection</u> ²
1.	Sulfuric Acid	128	525044	3895054	83	Yes
2.	Sodium Hydroxide (Caustic Soda)	95	185652	145173	83	Yes
3.	Xylene	92	230054	1800	83	No
4.	Poylchlorinated Biphenyls	92	6686	149	83	Yes
5.	Benzene	91	10836	400	83	Yes
6.	Ammonia	85	121847	181095	83	Yes
7.	Toluene	81	80616	26500	83	No
8.	Hydrochloric Acid	63	99896	635	83	Yes
9.	Styrene	59	136900	68563	83	No
10.	Chlorine	35	14897	—	83	Yes
11.	Cresol	33	586	—	83	No
12.	Phenol	26	19896	99	83	No
13.	Ethylene Glycol	23	8826	375	83	No
14.	Phosphoric Acid	22	31140	10210	83	No
15.	Formaldehyde	17	29340	90000	83	Yes
16.	Cyclohexane	17	3909	—	83	No
17.	Methyl Chloride	15	290	3440	83	No
18.	Acetic Acid	13	1010810	—	83	Yes
19.	Acrylonitrile	12	105396	228880	83	Yes
20.	Tetrachloro- ethylene	12	1355	99	83	No
21.	Acetone	11	3753	—	83	Yes
22.	Ethyl Acrylate	11	305	—	83	Yes
23.	Methanol	11	1262551	—	83	No
24.	Acrylic Acid	10	9680	125	82	Yes
25.	Napthalene	10	22635	—	82	No

NOTES: 1. Source of data - Coast Guard Pollution Information Response System (PIRS).

2. Level A protective clothing determinations based on findings in reference [2].

TABLE 3

MATERIAL-CHEMICAL COMPATIBILITY RECOMMENDATIONS
FOR SOME REPRESENTATIVE HAZARDOUS CHEMICALS [5]

Chemical	BUT	NAT	NPR	NIT	PET	CPE	PUR	PVA	PVC	VIT
Acetic Acid	R	rr	RR	RR	RR	r	R	n	RR	rr
Acetonitrile	—	r	r	—	—	—	—	—	—	—
Carbon Disulfide	nn	N	N	NN	nn	NN	r	RR	N	RR
Diethylamine	r	n	n	NN	r	—	r	n	n	n
Diethyl Ether	r	n	NN	rr	r	r	R	RR	N	n
Dimethyl Formamide	RR	NN	NN	NN	r	—	n	NN	N	n
Ethyl Acrylate	r	—	—	—	—	NN	—	—	n	NN
Freon TF	n	NN	RR	RR	NN	—	—	nn	NN	—
Hexane	NN	N	RR	RR	nn	r	R	RR	N	RR
Methanol	R	rr	rr	RR	r	r	r	NN	NN	RR
Methyl Ethyl Ketone	RR	NN	NN	NN	NN	n	N	NN	NN	NN
Oleum	r	—	rr	rr	n	r	n	n	rr	rr
Sodium Hydroxide	r	RR	RR	RR	r	r	r	n	RR	rr
Tetrahydrofuran	n	NN	NN	NN	NN	NN	n	NN	NN	n
Toluene	NN	NN	NN	nn	NN	n	r	rr	NN	RR

MATERIAL STATISTICS

	BUT	NAT	NPR	NIT	PET	CPE	PUR	PVA	PVC	VIT
No Rating	1	2	1	2	3	3	3	2	1	2
Positive Rating (R's)	9	4	7	7	6	6	8	5	3	8
Negative Rating (N's)	6	10	8	7	7	7	5	9	12	6

NOTES: 1. For explanation of recommendation codes (e.g., RR, R, NN, etc. see Table 4A)

2. These compatibility recommendations are for illustrative purposes only and should not be used for selecting protective clothing in hazardous chemical response.

TABLE 4

MATERIAL-CHEMICAL COMPATIBILITY RECOMMENDATIONS
BY CHEMICAL CLASS [5]

	BUTYL	NAT. RUB.	NEOPRENE	NEOP-SBR	NEOP/NAT. RUB.	NITRILE	NITRILE PVC	PE	CPE	PU	PVA	PVC	SBR	VITON	OTHER MATERIALS
Acids, Carboxylic															
• Aliphatic and Alicyclic															
— Unsubstituted	R	**	RR	r	r	RR	r	r	r	r	n	RR	**	r	
— Polybasic	**	RR	RR			RR	r	r	r	r	n	RR	**	r	
Aldehydes															
• Aliphatic	R	**	**			**	**	r	**	r	n	r	r	n	
• Aromatic and Heterocyclic	r	**	**	n	**	N	n	r	**	n	r	N		n	
Amides, Carboxylic															
• Aliphatic	r		NN			NN		**		NN				NN	
Amines															
• Aliphatic and Alicyclic															
— Primary	r	**	r			RR	r	r	NN	r	r	r	**		
— Secondary	r	n	r			**	**	**	NN	r	r	**	**	**	
— Tertiary	r	r	R	r	r	RR			r	r	r	RR		n	
Esters, Carboxylic															
• Aliphatic															
— Acetates	r	NN	NN	n	**	NN	n	**	NN	r	RR	NN	n	n	
— Higher Monobasic	r											N			
• Aromatic															
— Phthalates	**	**	RR	r		RR					**	**		**	
Ethers, Aliphatic	r	NN	**		**	RR					RR	NN		**	
Halogen Compounds															
• Aliphatic															
— Unsubstituted	NN	NN	NN	n	NN	NN	n	NN	NN	NN	**	NN	n	RR	FEP or TFE (RR)
— Substituted	**	**	**		**	NN		NN	NN	NN	**	NN			
• Aromatic															
— Unsubstituted	n	N	N			**	r	NN	**			N			
— Substituted	r	RR	RR			r					NN	r			
— Polynuclear	**	N	**		**	r					NN	RR	N		
Heterocyclic Compounds															
• Epoxy Compounds	r	n	**			**		**	**	NN	NN	n		n	
— Furan Derivatives	n	**	**		NN	NN	n	NN	NN	n	**	NN		n	
Hydrazines	**	**	**			**		**	**			**		**	
Hydrocarbons															
• Aliphatic and Alicyclic	NN	NN	RR	n	NN	RR	n	NN	r	R	RR	NN	n	RR	
• Aromatic	NN	NN	*	n	NN	*	n	NN	*	*	RR	NN	*	RR	
Hydroxyl Compounds															
• Aliphatic and Alicyclic															
— Primary	RR	**	RR	**		RR	r	r	r	r	**	**	**	r	
— Secondary	**	RR	RR			RR	r	r	r	r	RR	RR		r	
— Polyols	r					RR					RR	RR	**		
• Aromatic	r	**	RR		**	**	**	**	r	**	NN	**		**	
Inorganic Gas	r	n	R			n			r			**		**	
Inorganic Salts															
Inorganic Acids	**	**	**	n	**	**	**	r	**	r	NN	**	**	r	Saranex (r)
Inorganic Base	R	RR	RR	r		RR	r	r	r	r	n	RR	r	**	
Ketones, Aliphatic	r	NN	NN	n		NN	n	**	n	**	**	NN	r	NN	
Nitro		r													
— Unsubstituted	**	NN	**			NN		NN	NN	NN	RR	NN		NN	
Organo-Phosphorus Compounds	r		**			r				**				**	
Peroxides	r	**	RR			RR				r		RR		r	
Vinyl Halides									**						

Note: For explanation of recommendation codes (e.g. RR, R, NN, etc. see Table 1a). Class recommendations only for chemical classes in which two or more chemicals have recommendations for a given material. Double asterisks (**) indicate a wide variation in ratings within the class for the given material.

TABLE 4A

RATING CODE DESCRIPTIONS FOR TABLES 3 AND 4

Character	Performance Data	Vendor Recommendations
RR	Breakthrough times greater than one hour reported by (normally) two or more testers.	A or B ratings from three or more (apparently independent) vendors.
R	No Data	Same as RR
rr	Some data suggesting breakthrough times of approximately an hour or more.	A or B ratings from less than three vendors; no C's or D's.* B and C ratings — with B's predominating — from several vendors.
r	No Data	Same as rr
NN	Breakthrough times less (usually significantly less) than one hour reported by (normally) two or more testers.	C or D ratings from three or more (apparently independent) vendors.
N	No Data	Same as NN
nn	Some data (usually from immersion tests) suggesting breakthrough times greater than one hour are not likely.	C or D ratings from less than three vendors.* B and C ratings — with C's predominating — from several vendors.
n	No Data	Same as nn

*Products of some materials (e.g., CPE and Viton) are manufactured and rated by only one or two vendors.

TABLE 7

BREAKTHROUGH TIMES OF SAMPLE MIXTURES
FOR REPRESENTATIVE PROTECTIVE CLOTHING MATERIALS [13]

A. Acetone and Hexane Mixtures for Viton/Chlorobutyl Laminate

<u>Percentage Acetone</u>	<u>No. Runs</u>	<u>Breakthrough Time (min)</u>
100	7	53-61
95	1	0-5
86	1	6-11
50	5	2-6
35	2	0-6
15	1	6-11
5	1	0-5
1	1	0-5
0 (100% Hexane)	4	no BT (3 hrs.)

Breakthrough times reported for both acetone and hexane

B. Methylene Chloride Mixtures for Viton/Chlorobutyl Laminate

<u>Percentage CH₂Cl₂</u>	<u>No. Runs</u>	<u>Breakthrough Time (min)</u>	
		<u>CH₂Cl₂</u>	<u>Hexane</u>
In Hexane:			
100	1	25-36	—
50	2	42-47	57-62
0 (100% Hexane)	4	—	no BT
In Toluene:			
			<u>Toluene</u>
100	1	25-36	—
50	1	45-55	58-66
0 (100% Toluene)	1	—	no BT

TABLE 8

PROSPECTIVE SUIT MATERIAL PERMEATION BREAKTHROUGH TIMES
FOR VARIOUS SELECTED CHEMICALS

Chemical	Breakthrough times (minutes) ¹		
	Viton/CB	Butyl Rubber	CPE ³
Acetaldehyde	30-40	—	30
Acetic Acid	No BT	No BT ²	No BT
Acetone	95-98	No BT	20-25
Acetonitrile	90-105	No BT	70-80
Benzene	—	—	71-75
Carbon Tetrachloride	—	—	No BT
Chloroform	No BT	15	30-35
Cyclohexane	—	—	No BT
Dimethyl Sulfoxide	No BT	—	No BT
Ethyl Acetate	—	—	58-70
Ethyl Acrylate	14-32	34-45	65-70
Hexane	No BT	No BT	No BT
Isopropanol	—	—	No BT
Lindane in Chloroform	No BT	—	0-10
Lindane in Xylenes	No BT	80-90	—
Methanol	No BT	No BT	No BT
Methylene Chloride	25-36	0-1	15-25
Methyl Ethyl Ketone	25-40	—	28-35
Petroleum Ether	—	—	No BT
Styrene	No BT	—	60-70
Tetrahydrofuran	9-11	7-14	27-39
Trichlorotrifluoroethane (Freon TF)	No BT	35-40	No BT
Toluene	No BT	0-6	69-75

NOTES: 1. Breakthrough times measured using ASTM F 739-81 Standard Method with a Gas Chromatograph/Flame Ionization Detector (approximate sensitivity - 1 ppb).

2. "No BT" denotes no breakthrough within three hour period.

3. The materials tested were as follows:

- Viton/CB - Viton/chlorobutyl laminate; 5 oz/yd viton (outer or exposed surface), polyester, and 5 oz/yd chlorobutyl rubber (inner surface); 14 mil total thickness.
 - Butyl rubber - nylon butyl cloth as per Military Specification Mil-C-12189 (13 mil thickness)
 - CPE - Chlorinated Polyethylene, 30 mil thickness, unsupported
4. These reported breakthrough times are for illustrative purposes only and should not be used for selecting protective clothing in hazardous chemical response.

TABLE 9

PROTECTIVE CLOTHING MATERIAL PHYSICAL PROPERTIES AND TEST METHODS

<u>Characteristic</u>	<u>Test Method(s)</u>	<u>Requirement</u> ³
1. Weight (oz/yd ²)	FED STD 191,5051 ANSI/ASTM D751-79	25 (maximum)
2. Thickness (mil)	ANSI/ASTM D751-79	20 (maximum)
3. Breaking or Tensile Strength (lbs/in ²)	FED STD 191,5102 ANSI/ASTM D412-80 ANSI/ASTM 751-79	80 Warp (minimum) 80 Fill (minimum)
4. Tearing Strength (lbs/in ²)	FED STD191A,5134 ANSI/ASTM D751-79 ASTM D2261-80	9 Warp (minimum) 15 Fill (minimum)
5. Bursting Strength or Hydrostatic Resistance	FED STD 191,5312 ANSI/ASTM D751-79	200 (minimum)
6. Abrasion Resistance	FED STD 191,5302 FED STD 406,1091 H-18 Wheel, 600 cycles	no loose fibers
7. Puncture Resistance	NIOSH 77-134 ²	pass, no puncture
8. Flexibility	ASTM D1388-78 Flex 10 times, place in air fixture, check for air bubbles	pass, no air bubbles
9. Brittleness	ASTM D1790-62(1976)	pass at -25 F
10. Low Temperature Bending	ASTM D2136-66(1978)	pass at -25 F
11. Flammability	ASTM D1929-68	Self-extinguishing

NOTES: 1. Abbreviations:

ANSI - American National Standards Institute;
ASTM - American Society of Testing and Materials;
FED STD - U.S. Federal Standard

2. Test Method NIOSH 77-134; see Reference [16].

3. Requirements are recommendations the Coast Guard uses for evaluating Level A Encapsulated suit materials.

U.S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESPONSE TEAM
GENERIC ASBESTOS AIR MONITORING GUIDES FOR
HAZARDOUS WASTE SITES

by

Rodney D. Turpin, Safety and Occupational Health Manager
U.S. Environmental Protection Agency
Environmental Response Team
Edison, NJ

Jeff Pike, On-Scene Coordinator
U.S. Environmental Protection Agency, Region III
Philadelphia, PA

Kenneth M. Wallingford, Ralph H. Zumwalde, Rick Hartle
U.S. Department of Health and Human Services, NIOSH
Cincinnati, OH

Tim Travers
U.S. Environmental Protection Agency
Region III/Weston TAT
Pennsauken, NJ

Phil Campagna
Ecology and Environment, Inc.
Buffalo, NY

INTRODUCTION

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters, and Regional Offices as well as other government agencies in the area of emergency environmental issues such as chemical spills and uncontrolled hazardous waste sites.

This paper describes the methodologies currently being used and evaluated by the U.S. EPA-ERT, U.S. EPA Region III, and U.S. EPA Region III TAT for on-site, off-site, and residential air sampling. These tentative guidelines were developed with the assistance of the National Institute for Occupational Safety and Health (NIOSH), and Centers for Disease Control. The guidelines include a description of collection techniques and analytical methods which are used by the ERT and modified and improved each time they are implemented. The authors suggest you contact the ERT to obtain the latest modifications before you apply this evaluation criteria.

ASBESTOS

Asbestos is a generic term for the fibrous forms of special mineral silicates. Those asbestos minerals currently regulated by Federal agencies include, chrysotile, crucidolite, amosite, tremolite, actinolite, and anthophyllite. Asbestos has been used in many commercial products such as textiles, insulation, friction and cement products, because of its chemical and physical properties. Human exposure to all commercial asbestos types have been associated with high ratios of asbestosis, lung cancer, mesothelioma. Exposure to asbestos fibers can be found in many occupational settings and in the ambient air and water as a result of the use of asbestos products or release of asbestos from contaminated waste sites. An immediate concern of the ERT are those waste sites that are primarily comprised of waste asbestos products or asbestos tailings. These waste sites often range in size from a few acres to several square miles.

ON-SITE SAMPLES

I. Types of samples (Bulk and Air Samples).

A. Bulk sample (4 oz. container).

1. Sample location.

- a. Develop site specific sampling grid to collect a representative sample from different locations of the waste site.

2. Types of analysis.

- a. PLM (all samples) - for presence of asbestos - refer to appropriate methodologies for analytical procedure.
- b. SEM/TEM - select 1-4 of the positive PLM samples for characterization of asbestos fiber type.

B. Air samples.

Air sampling will be performed throughout the entire cleanup effort and be determined daily according to meteorological conditions.

1. Filter media.

- a. 25mm - 37mm mixed cellulose ester filter (0.45 um - 0.80 um pore size) using a 3-section cassette.

2. Sampling pump.

- a. Battery operated pumps should be capable of operating with the above filter media (B.1) at a flow rate of 2.0-4.0 Lpm. For those situations where concentrations to background particulates or asbestos fibers are thought to be low, an electric vacuum pump may be required that is capable of operating at a flow rate of 1 cfm.
- b. A Real-time Aerosol Monitor (RAM) field instrument may be useful in determining particulate sources, flow patterns, and relative concentrations on-site. This information may be useful in determining the initial flow rates since particulates concentration may cause pump overloading or analytical problems. The following suggested flow rates are based on our limited on-site experiences and should only be used to assist in selecting the site specific flow rate;
NOT AS A GUIDE:

	<u>LPM</u>
(1) Low real-time monitor readings: $< 6.0 \text{ mg/M}^3$	<u>11-17.6</u>
(2) Medium real-time monitor readings: $\geq 6.0 \text{ mg/M}^3$	<u>7.5</u>
(3) High real-time monitor readings: $\geq 10 \text{ mg/M}^3$	<u>2.5</u>

3. Analytical methods

- a. All on-site samples collected will be analyzed by PC. (Refer to appropriate NIOSH Method 7400.)
- b. As a minimum, duplicate samples will be collected at 10% of the on-site air stations.

C. Weather conditions for air sampling using the 3 section cassette.

1. Minimum of 36 hours to 3 days of dry weather before sampling; and
2. Wind speed of approximately 10 mph or greater during sampling; and
3. Soil condition should be dry/non-moist at time of sampling.

D. Sampling stations and samples per day.

1. Minimum of 6 sampling stations.

- a. Two stations will be within the work area. One station will be upwind of work area on property line, and two stations will be downwind of work area on property line. Another station will be situated between work area and downwind stations.
2. At a minimum, 2 samples (3 section cassette, cellulose ester filter) should be collected at each work site. Anticipate collecting samples for a minimum of 6-8 hours each.
3. If site cleanup activities are underway, a minimum of 4 sampling screening with the RAM (e.g., 2 times in the A.M. and 2 times in the P.M.) should be taken to assist in determining the effectiveness of the dust control techniques.

AMBIENT AIR SAMPLING OFF-SITE

- I. Screen area with real-time aerosol or particulate instrument(s).
 - A. In some situations, it may be useful to use a RAM or similar instrument to determine airborne background contamination. These measurements may be useful for identifying sites for asbestos samples.
- II. Sample collection.
 - A. Types of analysis - duplicate samples are collected at each station (X, Y).
 1. Analyze all (X) samples from each station by PC. Refer to appropriate NIOSH methodologies for analytical procedures. (Certified approved/NIOSH laboratory.)
 2. Analyze a minimum of 25% of those air samples that are evaluated by the PC method and have a reportable quantity of 0.04 fibers/cc or greater.
 - a. TEM with Selected Area Electron Diffraction (SAED) or
 - b. SEM with Energy Dispersion X-ray Analysis (EXDA).
 3. Analyze a minimum of 10% of those air samples that are evaluated by the PC method and have a reportable quantity of 0.04 fibers/cc or less.
 4. If site conditions deem it necessary, determine if bulk samples contain asbestos using PLM (See Section 1,A,1,a; Section 1,A,2, a and b.

REMEMBER: The primary objective of this sampling scheme (when collecting airborne samples) is to collect a sufficient volume of air to obtain a detection limit of 0.001 fibers/cc with the confidence level being 0.04 fiber/cc. (Refer to NIOSH Method 7400).

B. Sampling grid (station location).

1. Positive RAM readings.

a. Maximum 500 feet downwind from site.

b. Minimum of 1-2 samples per 1000-2000 feet perpendicular to wind direction adjacent to site.

(1) If site conditions do not register positive responses above background on the RAM field instrument, then sample station locations should be based on other factors (e.g., wind direction, wind speed, building structure.)

2. Background stations.

a. Minimum of 3 stations.

b. Angles are 45°, 90°, and 135°; 500 feet to 1 mile upwind of the site.

(1) Off-site survey should assure that background stations will not be interfered by off-site sources of asbestos (e.g., auto brake shops, heavy traffic) or dust in general (dirt roads, etc.).

C. Sampling methodology at each station.

1. Filter media - (See Section I,B,1).

2. Possible flow rates.

a. Low flow pumps (per station).

(1) 2.0-4.0 l/min for 500-1500 liters.

b. High flow pumps applicability and location, to be determined per-site.

(1) 7.45 liters/min for 1000-2000 liters.

(2) 11-17.5 liters/min for 1000-3000 liters.

(a) Not to exceed 1 cubic foot per minute.

D. Weather conditions for air sampling.

1. Minimum of 36 hours to 3 days of dry weather before sampling; and
2. Wind speed approximately 10 mph or greater during sampling; and
3. Soil condition should be dry/non-moist at time of sampling.

RESIDENTIAL - Non-Commercial Buildings (if applicable)

I. Screening - will be conducted at randomly selected residences directly adjacent to the disposal pile.

II. Selected areas for settled dust sampling within the residential environment.

A. Static areas (undisturbed areas).

1. Attic, rafters, basement, crawl space, etc. (ascertain type insulation or asbestos that may be used.)
2. Garage.

B. Living areas (undisturbed areas).

1. Behind and/or underneath appliances, i.e., refrigerators, stoves, etc.
2. Light fixtures.
3. Embedded in perimeter of carpet (under tables, couch).
4. Surface areas of drapes.

III. Sampling design.

A. Since the emphasis is to qualitatively assess exposure, the primary effort should be directed towards identifying the presence of asbestos. This could best be achieved through the collection and analysis of settled dust. This should be accomplished by:

1. Selecting areas as defined in B, 1 and 2. These areas should be measured so as to allow determination of fiber concentration per area sample. These types of measurements may be useful for comparison purposes.

IV. Sample apparatus.

- A. Battery operated sampling pump capable of 2.0 to 4.0 liters per minute flow rate using filter media and 3-section cassette discussed in I,B,1.

V. Sample procedures.

- A. The attempt is to collect settled dust from exposed surfaces onto the filter media.

1. The area to be selected, measured and sampled will vary depending on the amount of "free" dust on the surfaces. The person collecting the sample will need to make this assessment.

- a. Since the sample should not be overloaded or underloaded, the following may be used as general guides to determine sampling area. The purpose of the sampling area is to identify the appropriate sample load if additional sampling is required:

Heavily visible settled dust: (a) 10 cm^2 - 50 cm^2 at 2 1/min

Moderately visible settled dust: (a) Approx.:
 50 cm^2 at 3-4 1/min

Lightly visible settled dust: (a) Approx.:
 75 cm^2 at 4 1/min

No visible settled dust: (a) Approx.:
 100 cm^2 at 4 1/min

Since it will be difficult to determine the amount of settled dust present, it may be applicable to collect progressionary samples (i.e., 10 cm^2 , 20 cm^2 , 50 cm^2) in the same general area but at different locations.

- b. A sample holder or cassette should be used in which the surface of the filter is at a minimum of 1/4 inch above the top of the surface. The height of the sampling cassette above the surface should be the same during all phases of sampling.

The sample holder or cassette should be open faced and placed in contact with the surface to be sampled, e.g., the rim of the open faced cassette that contacts the surface should be notched to allow for reduced pressure buildup on the pump.

With the pump turned on, sample holder should be moved across the surface making sure the total defined area is sampled. Depending on the filter loading, repeated sampling across the

same area may be warranted. Should the investigator decide that more particulate material is needed for proper filter loading, additional areas can be defined and measured for sampling. Using the same filter and procedures these areas should be likewise sampled. All areas sampled should be physically measured and recorded by the investigator.

VI. Sample Analysis.

A. Optical Microscopy.

1. Filters should be prepared and analyzed by the most current NIOSH methodology by Phase Contract Microscopy (NIOSH Method 7400).
2. Concentration of fibers should be determined for unit area measured.

These fiber data should be used for comparison purposes in this study to assess extent of contamination and for making decisions for additional sampling and analysis.

B. Electron Microscopy.

1. A representative number of samples should be selected for fiber identification by either Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). These microscopy methodologies should be used for fiber count and also identification of the fibers, using Selected Area Electron Diffraction (SAED), TEM only, and/or Energy Dispersive X-Ray Analysis (EDXA) (SEM or TEM).

These data can be used for comparison with optical fiber counts and to ascertain the presence of asbestos. It may be possible to determine if asbestos contamination is the same type of fiber identified from the nearby waste site.

2. Soil surface samples collected near the residents should be prepared and analyzed using Electron Microscopy.

CONCLUSION

A site specific asbestos monitoring plan must incorporate a daily/routine site monitoring; employee sampling, and an emergency plan. The specifics for these plans are not included in the objectives of this paper since they are site specific and are less likely to be modified. It is the hope and desire of the authors that this paper will assist others involved with state-of-the-art techniques for monitoring asbestos at asbestos tailing piles at hazardous waste sites.

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- (TEM) - Transmission Electron Microscopy
- (SEM) - Scanning Electron Microscopy
- (PC) - Phase Contrast Microscopy
- (RAM) - Real Time Aerosol Monitor
- (PLM) - Polarized Light Microscopy

EVALUATING THE EFFECTIVENESS OF CHEMICAL PARAMETER SPECTROMETRY IN ANALYZING VAPORS OF INDUSTRIAL CHEMICALS

by

J.R. Stetter, W.R. Penrose, S.Z. Zaromb, D. Christian,
D.M. Hampton, M. Nolan, M.W. Billings, C. Steinke, and T. Otagawa
Energy and Environmental Systems Division,
Environmental Research Division,
Argonne National Laboratory
Argonne, Illinois 60439
and
Lt. J.O. Stull,
U.S. Coast Guard, Office of Research and Development
Washington, D.C.

1. BACKGROUND

We have previously reported the development and testing of a device based on "Chemical Parameter Spectrometry (CPS)."¹ This is a generic name for an analytical technique that combines the inputs from several sensors with built-in computerized pattern matching and can perform qualitative and quantitative analysis simultaneously. In principal, the method will work for any grouping of sensors, from two to any arbitrary number.

The first application of this technique was focused on the needs of the United States Coast Guard, whose personnel may be exposed to the vapors of industrial chemicals both occasionally, in spill situations, and chronically, in routine inspections of commercial vessels. The system was designed to protect the health and safety of these workers. Chemical vapors can be detected, identified, and monitored rapidly in a small rugged instrument. The specifications for this monitoring device are shown in Table 1.

2. INSTRUMENTATION AND METHOD

After screening available detection technologies for the hazardous chemicals of interest, an array of three-electrode amperometric (electrochemical) cells was selected as the primary detector. These cells are simple, inexpensive, and rugged. On the other

TABLE 1 Initial Specifications: Hazardous Vapor Detector for the United States Coast Guard

Requirements: A device that will

- respond to a variety of chemicals
- identify most hazardous compounds by name
- measure concentrations of 1 to 50000 ppm in air
- operate in various and fluctuating environments
- be reliable and accurate
- alarm when hazardous levels are exceeded

in an instrument package that is:

- truly portable (<15 lb)
 - simple to operate and maintain
 - rugged
-

TABLE 2 Compounds Tested for Response to the Prototype Chemical Parameter Spectrometer at PPM Levels

1. Hydrogen Peroxide (7.5-300 ppm)	21. Toluene (100 ppm)
2. Ethyl Acrylate (20-100 ppm)	22. Trichloroethylene (300 ppm)
3. Pyridine (15-150 ppm)	23. Acetone (50 ppm)
4. Nitrogen Dioxide (6-48 ppm)	24. Tetrahydrofuran (100 ppm)
5. Sulfur Dioxide (9-80 ppm)	25. Chloroform (100 ppm)
6. Chlorine (9.5-189 ppm)	26. Nitromethane (100 ppm)
7. Formaldehyde (3.75-100 ppm)	27. Acetic Acid (100 ppm)
8. Nitrobenzene (7.5-300 ppm)	28. Benzene (100 ppm)
9. Benzyl Chloride (50 ppm)	29. Ammonia (30 ppm)
10. Aniline (400 ppm)	30. Cyclohexane (300 ppm)
11. Acrylonitrile (204 ppm)	31. Carbon Monoxide (200 ppm)
12. Sulfuryl Fluoride (75 ppm)	32. Vinyl Acetate (40 ppm)
13. Hydrogen Cyanide (165 ppm)	33. Formic Acid (40 ppm)
14. Hydrazine (15 ppm)	34. Nitrogen Oxides Mixture (20/20 ppm)
15. Methane (12,000 ppm)	35. Boron Trifluoride (700-30,000 ppm)
16. Ethyl Alcohol (150 ppm)	36. Monomethylhydrazine (15 ppm)
17. Hydrogen (200 ppm)	37. Methyl Isocyanate (10-200 ppm)
18. Nitric Oxide (60 ppm)	38. Unsymmetrical Dimethylhydrazine (15 ppm)
19. Hydrogen Sulfide (83 ppm)	39. Benzoyl chloride (5-50 ppm)
20. Carbon Tetrachloride (100 ppm)	40. Diethyl ether (100 ppm)

hand, they are also insensitive to many compounds of interest, especially the simple aromatic organic compounds like benzene, and they are more subject to drift, fatigue, and nonreproducibility than some other detectors.

By exposing the incoming gas samples to a heated noble metal filament, these electrochemical cells can be made to respond to a wide variety of non-electrochemically active compounds.² With computer control of the filament temperature, it appears that the spectrum of partial oxidation or pyrolysis products is characteristic of each compound and not significantly dependent on concentration, interferences, and humidity.³ Each of the approximately 40 compounds tested so far yields a unique response in this system (Table 2). These compounds include S-, N-, O-, and C- containing organic and inorganic vapors as well as room-temperature gases like CO, NO, NO₂, H₂S, SO₂, and HCN. Negligible response is obtained from the normal constituents of clean air (O₂, N₂, CO₂ and argon) using this particular sensor array.

The instrument is shown in Figure 1 and a schematic diagram of its internal organization is shown in Figure 2. Four electrochemical cells are placed serially in the sample stream, in order of increasing sample consumption. They are biased at different working electrode potentials and use different working electrode materials to give distinct responses to the various chemical vapors.

In order to identify vapors using this approach, the instrument is operated sequentially in four different modes (Table 3), controlled by the computer. In each mode, the responses of the sensors are recorded, and at the end of the sequence, the computer has stored a set of 16 numbers, each corresponding to one of the four sensor signals in one of the four modes.



FIGURE 1 Photo of CPS-100; 15 lbs, 6" x 7" x 9", rechargeable battery, LCD readout, plus alarm, with pushbutton operation

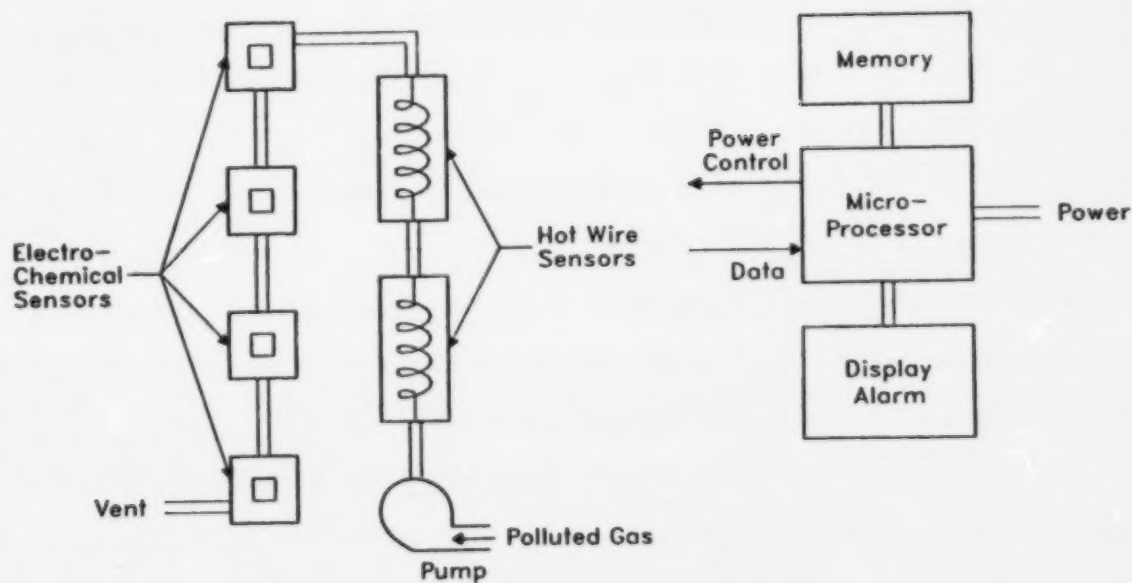


FIGURE 2 Schematic Diagram of CPS-100

A difficulty with electrochemical cells is their repeatability and accuracy. The question is: can the redundancy in 16 numbers plus the availability of the onboard computer overcome the problems inherent in electrochemical cells? In the case of this instrument, the answer has been "yes".

The pattern-matching algorithm listed in Table 4 is programmed into the instrument. It is relatively simple and makes economical use of the limited computing time and space available in a portable instrument. Yet, it is quite powerful. The 16 numbers obtained by the identification algorithm data collection scheme are treated as a 16-element vector, i.e., as a point in 16-dimensional space. The unknown vector is first normalized to eliminate the concentration dependence of the raw sensor signals. Then the Euclidean distances are calculated between the unknown vector $\bar{u}$ and each pattern vector $\bar{p}$ in the computer's library. The compound identified is the one with the shortest distance between $\bar{u}$ and $\bar{p}$ and it is displayed on the LCD readout (see Figure 1). The identification information is used to select a concentration coefficient from those stored in memory. The gas concentration is calculated and displayed using the sensor that has the most sensitive response to the particular gas. Thus, the qualitative and quantitative analysis is complete in about 4 minutes using the present scheme.

It is important to know the reliability of any analytical measurement that is used to make a decision regarding health and safety. Reliability is estimated in two ways, both of which are reported to the operator via the LCD readout. First, reliability is inversely related to the minimum Euclidean distance. An ideal identification has a distance of zero between the unknown vector $\bar{u}$ and the pattern vector $\bar{p}$. Distances of under 30 units have been found to yield unambiguous identification when selecting one compound from a group of approximately 16 chemicals.

A second measure of the reliability of this analysis is a parameter that we call "close matches." These are all the compounds whose pattern vectors fall within a

TABLE 3 Operating Modes and Channel Numbers for IDENT Mode

Mode	Cell No:	1	2	3	4
	Working Electrode: Bias:	Au -100 mV	Au +300 mV	Pt +200 mV	Pt Black 0 mV
Pt filament, 900°, 54 sec		1	2	3	4
Rh filament, 900°C, 42 sec		5	6	7	8
Rh filament, 1000°C, 35 sec		9	10	11	12
no filament, 30 sec		13	14	15	16

TABLE 4 Identification Algorithm

1. Acquire 16-element unknown vector $\bar{u} = \{u_1, u_2, \dots, u_{16}\}$.
2. Normalize $\bar{u}$ so that largest element is +127 or -128.
3. Calculate Euclidean distance D between $\bar{u}$ and each known pattern vector, using weighting vector $\bar{w}$.

$$D = \sqrt{w_1(u_1 - p_1)^2 + w_2(u_2 - p_2)^2 + \dots + w_{16}(u_{16} - p_{16})^2}$$

4. Choose the shortest distance. The corresponding $\bar{p}$ is the identification.
5. Find all distances less than twice the shortest distance. These are termed close matches.
6. Using the strongest channel of the identified pattern vector $\bar{p}$, calculate the concentration.
7. Calculate the percentage of the alarm level. Set the alarm if appropriate.

hypersphere with a radius that is twice the minimum Euclidean distance. The instrument reports both the number of close matches and their names since the actual compound may be one of these. The reliability of the information is high if there are no close matches and low if there are many possible misidentifications. In cases where low reliability is noted, the user must obtain better sample data or send the sample to be analyzed in a laboratory.

3. INSTRUMENT EVALUATION

A method for evaluating the operation of the instrument and the reliability of the identification algorithm is to calculate the Euclidean distances between each possible pair of compounds in a library of pattern vectors. The shorter the distance between two compounds, the greater the likelihood of confusing one with another. An example of this approach is illustrated in Table 5 for six common compounds. Each of these was run three times and averaged to get the set of pattern vectors. These were then programmed into the instrument's library. The closest points in sixteen dimensional space are benzene and cyclohexane. The consequences of this closeness can be evaluated by running the six compounds again as unknowns (Table 6). Not surprisingly, benzene is frequently mistaken for cyclohexane, although the reverse is not true. Occasionally benzene and cyclohexane are confused with carbon monoxide, and the distances in Table 6 for benzene and cyclohexane from CO are 94 and 115, respectively. This is not quite far enough apart for unambiguous identification. Other gases like NO₂, where more than 360 counts separate it from any other chemicals, are never confused with the other gases in Table 6.

To test the limits of the instrument's identification capability, a set of 16 gases were selected from Table 2 and run repeatedly, and the numerical data, identification, reliability, and close matches were recorded. The data for each gas in each array were inspected, averaged, and normalized, then programmed as pattern vectors into the

**TABLE 5 Distances Within a Set
of Pattern Vectors for Six Compounds**

	CO	BZ	H ₂ S	NO ₂	CHX	SO ₂
CO	0	94	148	443	115	140
BZ	94	0	174	392	50	159
H ₂ S	148	174	0	461	185	127
NO ₂	443	392	461	0	361	468
CHX	115	50	185	361	0	175
SO ₂	140	159	127	468	175	0

BZ = benzene

CHX = cyclohexane

**TABLE 6 Close Matches and Actual
Misidentifications Using the Six
Six Compounds of Table 6**

Analyte Gas	Close Match	Actual Misidentifications
CO	none	none
BZ	CHX (CO)	CHX
H ₂ S	none	none
NO ₂	none	none
CHX	none (CO)	none
SO ₂	H ₂ S	none

() = very infrequent

library of the onboard computer. The 16 chemicals were then analyzed as unknowns in the instrument containing this library. This experiment was done on two arrays of cells (nos. 10 and 11) which were nearly identical.

The results of this evaluation are shown in Table 7 for two different arrays of four cells. Both arrays yielded similar reliabilities of identification using the unadorned identification algorithm (Table 7, line A). Different methods were used to try to "tune" the algorithm. First, in Table 7, line B, those runs were eliminated where any of the 16 signals was more than three standard deviations from the mean, or where any signal had the wrong sign and included obviously incorrect data. This caused significant improvement in the identification for array 11 only.

The second method applied a weighting vector to the data; this assigns a degree of importance to each channel. This method has the effect of stretching 16-dimensional space this way or that to attempt to even out the distances among the pattern vectors. Although there are ways to optimize the weight vector, in our experience these have been no more effective than simply inspecting the data to identify the channels with the largest between-compound variation and the smallest within-compound variation, and emphasizing the channels accordingly.

The effects of two different weight vectors are shown in lines C and D of Table 7. De-emphasis of the strongest channels (3, 4, 7, 8, 11, 12, 15, and 16) (line C) yields only a little improvement. On the other hand, emphasis of the last channel (line D) greatly boosts the identification ability of array 11. There is only one misidentification in 42 runs, and the number of potential errors (close matches) is very low.

A third way to improve identification is in careful selection of compounds incorporated into the library. For example, benzene and cyclohexane are sometimes confused with one another. With the elimination of cyclohexane from the library, the identification of benzene — the most toxic of the two by far — becomes much more

**TABLE 7 Summary of Compound Identification
Performance for Two Test Arrays AR10 and AR11**

Array 10					
Con- dition	# of Runs	# In- correct	# of Correct Idents	Correct with no Close Matches	# with Close Matches
A	62	10	52	25	27
B	51	7	44	19	25
C	51	9	42	23	19
D	51	26	25	14	11
Array 11					
Con- dition	# of Runs	# In- correct	# of Correct Idents	Correct with no Close Matches	# with Close Matches
A	48	8	40	27	13
B	42	4	38	32	6
C	42	3	39	29	10
D	42	1	41	37	4

A - All 62 runs included.

B - Reduced number of runs. Runs culled to eliminate obviously erroneous data.

C - Reduced number of runs, weight vector = 4,4,1,2, 4,4,1,2, 4,4,1,2, 4,4,1,2

D - Reduced number of runs, weight vector = 1,1,1,1, 1,1,1,1, 1,1,1,1, 1,1,1,10

reliable as far as the instrument is concerned. This does provide improved safety information by elimination of false negatives at the expense of increased false positives, i.e., the user could never find himself in toxic benzene vapors and get an identification as cyclohexane.

A fourth method to improve the separation of the gases so that unambiguous identification is more likely, is to carefully select the sensors that make up the array. It is obvious from the performance data presented in Table 7 that Array 11 is superior to Array 10. It happens that this is because sensor four in each array has a different reactivity among CO, benzene and cyclohexane. In array 11, the pattern vectors are more unique for each gas. This approach suggests that each array should be optimized for a given problem or set of chemicals to be analyzed.

CONCLUSIONS

We have measured in an actual prototype instrument the ability of chemical parameter spectrometry to identify individual vapors from among a set of 16 possible vapors. For a selected array, this has been accomplished 41 of 42 times or with 98% reliability. Also, the Euclidean distance reported by the instrument can give the user a measure of the reliability of an individual determination. A distance of 30 or less is indicative of a reliable identification and a near perfect match while distances larger than 100 give ambiguous data. Improvements are seen in the identification capability of an instrument by using arrays that are selected for specific problems and by using computer algorithms that obtain the maximum information from any individual array.

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DEVELOPMENT OF A PERSON-PORTABLE ANALYTICAL SYSTEM

Alan W. Underdown
Martha J. Townshend Colford
Underdown Chemometrics Limited
Nepean, Ontario

BACKGROUND

Following a chemical spill incident, implementation of effective response measures requires rapid and reasonably accurate determinations of the concentration of the spilled chemicals in air, water, and soil in the vicinity of the spill site (1). Measurements of concentrations in air are most critical immediately after a spill incident since the data are needed to make decisions on protection measures for both spill responders and the surrounding population. Measurements of concentrations in surface water and soil are important since these phases can provide pathways for transport beyond the immediate spill area. The data are useful in making decisions on protection measures, planning clean-up operations and assessing environmental damage. Recognizing that these analytical requirements were not adequately met in most spill situations, the Environmental Emergencies Technology Division (EETD) of Environment Canada undertook, in 1980, a development program for analytical methods suitable for spill response. This program is part of the Chemical Hazards Emergency Countermeasures (CHEC) program. Existing methods and instrumentation were reviewed and grouped into five classifications or levels, based on criteria of portability, accuracy and complexity. Levels 1, 2, and 3 were considered most appropriate for spill monitoring and EETD decided to actively pursue methods belonging to these levels. The levels are, as follows, Level I: Pocket-portable equipment (based on reagent colour changes), Level II: Person-portable detectors based on electronic detectors (meters), and Level III: Vehicle-portable instruments (normally found in a fixed laboratory and microcomputer technology to be used to simplify operation). In each case, the methods are to be suitable for use by personnel without extensive training in chemistry or analytical instrumentation methodology and working under emergency conditions. Development work on each of the three levels is warranted since they each have unique advantages. For instance, Level II instrumentation is more easily transportable than Level III instrumentation and will most likely require less maintenance and operator training. However, in most cases it will not be as accurate.

Initial work on the Level II project involved evaluating a wide range of commercially available instruments and methods. In choosing equipment to adapt to the spill site monitoring program, accuracy, ease of use, and the capability to analyse a large number of the chemicals on the priority substances list, which was developed by EETD in 1982 (1), were considered as important criteria. Air monitoring instruments which satisfied these criteria were the Foxboro Model 128 Organic Vapour Analyser (OVA) and the HNU System Inc. PI-101 Photoionization Analyser (HNU). The HACH DR-EL/4 Environmental Portable Laboratory (Hach Kit) was the most promising candidate for development to satisfy the Level II criteria for water and soil analysis. Accordingly, work to date has focused on the OVA and HNU for air analysis, and the Hach Kit for water and soil analysis.

In this paper only a brief description of the Level II instruments is given. For a more detailed description of the OVA 128, the HNU PI-101 and the Hach DR-EL/4, one should refer to Lockwood and Halman (2) and Halman et al. (3).

OVA 128

This instrument is basically a portable flame ionization detector (FID). In operation, a continuous metered flow of sample air is drawn into the detector chamber where organic molecules are burned in a hydrogen flame, producing positively-charged carbon-containing ions. These ions are driven to a negatively-charged collector electrode where a current is generated which is proportional to the ion collection rate. This current is measured with a pre-amplifier, the output signal from which is further amplified and displayed on the meter assembly situated on the hand-held probe assembly. The detector exhibits inherently high sensitivity and responds to a wide range of organic chemicals. The OVA has its own hydrogen supply and rechargeable 12V DC battery allowing for a minimum of eight hours of continuous operation.

HNU PI-101

This instrument is basically a portable photoionization detector (PID). In operation, a continuous flow of sample air is drawn by a DC-operated fan into an ionization chamber located on the hand-held probe. Photons emitted by the 10.2eV UV source pass through a transmitting window into the ionization chamber where this radiation is absorbed by molecules having ionization potentials of approximately 10.2eV or less. The positive ions produced are driven to a collector electrode, where a current proportional to the concentration of the sample substance in air is generated. This current is amplified and used to drive a meter on the readout unit. The HNU is a selective detector, since chemicals having ionization potentials much greater than 10.2eV will not be ionized and therefore will not produce an instrument response. The HNU is capable of detecting a broad range of organic compounds, as well as a few inorganic compounds (e.g. H_2S and NO_2). Similar to the OVA, the HNU utilizes a rechargeable battery which allows for 10 hours of continuous service.

HACH DR-EL/4

The Hach Kit is a portable laboratory containing a Spectrophotometer/Conductivity meter, a pH meter, a digital titrator, and premeasured reagents, which are used to carry out analysis for many inorganic chemicals in water, including those on the EETD priority list (1). These wet-chemical analyses can be reliably performed by non-technical personnel. With the exception of phenol, however, there are no methods for organic chemicals.

PREVIOUS EXPERIMENTAL WORK

Initial efforts were directed towards performance evaluation of the instruments described in the previous section. A summary of the initial findings includes the following:

- 1) The sensitivity and ease of use of the OVA and HNU make them suitable for use at spill sites.
- 2) Responses of these instruments are fairly stable and reproducible but the response factors determined are not always in agreement with those supplied in the literature by the manufacturer. In addition, the response of the instrument is not always linear over the ranges of interest.
- 3) Several maintenance problems occurred with the instruments which were not adequately covered by the manufacturers' documentation.
- 4) The instruction manuals provided with both the OVA and HNU are not appropriate for use as field manuals by spill responders. Shorter, more easily read documents are needed.

Based on these findings, further experimental work was undertaken to produce accurate calibration data for as many compounds as possible from the EETD priority list of spilled chemicals (1).

RECENT DEVELOPMENTAL WORK

Recent efforts have been directed towards bringing the OVA and HNU work to the "field-ready" stage and to continue the developmental work on the Hach Kits. The following tasks have either been completed or are currently underway:

- 1) Completion of calibration experiments for the EETD priority list chemicals on the OVA and HNU instruments.
- 2) Several studies on factors which affect the accuracy of readings from these instruments and which are relevant to spill site conditions.
- 3) Conversion of the OVA and HNU calibration data to a form usable by spill responders (i.e. meter scale overlays and primary calibration procedures).
- 4) Development of field manuals for the OVA and HNU instruments. These manuals will be used with the meter scale overlays and associated primary calibration procedures.
- 5) A comprehensive literature search of methodologies for analysis of organic compounds in soil and water which can be used with a modified Hach DR-EL/4 kit.
- 6) Experimental work to evaluate promising methods for analysis of organic compounds in soil and water and, if possible, to modify the existing Hach Kit to comply with the Level II criteria.

OVA AND HNU CALIBRATION DATA

In order to produce reliable data on the response of the OVA and HNU to specific chemicals, it was necessary to prepare accurate concentrations of these substances in a safe and convenient manner. The methodology for chemicals which are normally liquids, was developed by the previous contractor and tested extensively for accuracy (2,3). It involved injection of a known quantity of the chemical into a bag of flexible, inert material (Tedlar) containing an accurately measured quantity of ultrapure air. After evaporation and thorough mixing was completed, air was sampled by several instruments within a short time period. Measurements were taken in a narrow temperature range (24-26°C) and sufficient time was allowed during each measurement to produce a fairly constant result (<2% drift/minute). Readings for most substances became stable after a few seconds, but several minutes were needed for some of the higher boiling point liquids (B.P.>100°C). During all calibration experiments, instrument sensitivity was adjusted using the primary calibrant substance for each instrument (e.g. benzene for the HNU and methane for the OVA). In each case, instrument sensitivity was adjusted to read close to the nominal concentration of a commercial standard (e.g. 101 ppm benzene or 93 ppm methane) at the beginning of each day of experimental work. Readings of standards were recorded periodically.

In this study, we continued the calibration work on the priority list of chemicals using the above-mentioned method. We repeated experiments on several compounds studied previously by Lockwood and Halman (2, 3) and obtained agreement within the instrument-to-instrument variability (<10%).

In addition to the chemicals which are liquids under ambient conditions, we also studied several gaseous compounds. In these studies, the sample preparation method was modified slightly to include the introduction of known quantities of gases from lecture bottles. This was done by drawing the gas from a flowing stream into a gas sampling syringe which was then emptied into the Tedlar bag.

The range of concentrations studied for each chemical was determined by factors such as toxicity limits (e.g. TLV, IDLH) and the vapour pressure. Sufficient data in each case was collected to provide a statistical analysis of instrument response and to determine the shape of the response vs. concentration curve. In the following section, several factors which can influence both the accuracy of experimental work and field measurements will be discussed. Presently, we feel that sampling static test atmospheres in the Tedlar bags is the best way to measure instrument response as a function of concentration in the absence of any perturbing effects. The effects of factors such as temperature, sampling time, and wind on the instrument response can then be studied separately and taken into account when evaluating the accuracy of field instruments.

The temperature dependences of OVA and HNU response was investigated by carrying out calibration experiments in a walk-in environmental chamber under constant temperature. HNU responses to benzene were measured between 4°C and 32°C. HNU responses were found to be temperature-independent over the experimental range. OVA responses varied inversely with temperature. Table (2) summarizes the results of the temperature study.

In carrying out the calibration work, a primary concern has been the linearity of response over the range of concentrations of interest. Linear response would be desirable since it would simplify both laboratory calibration and field measurement aspects. Unfortunately, experimental work done under this and last year's contract indicates that inherent deviations from linearity occur with both instruments (2, 3). Figures (1) and (2) show instrument response vs concentration curves for the OVA and HNU respectively. HNU sensitivity is a decreasing function of concentration. Results for the OVA indicate variations in sensitivity with concentration if data from all three ranges are taken together. Another approach is to consider the data from each range separately. By using linear regression, we found that the data for the x1 and x10 ranges taken together conformed very well to a straight line in almost all cases, but a better fit was obtained when data from the x100 range was fit separately. Using this approach, good correlation coefficients were obtained as summarized below:

x1, x10 ranges	.9981	- average of results on 51 substances
x100 range	.9975	- average of results on 51 substances

Another key factor which can influence both the accuracy of experimental work and field measurement is variability in response from instrument to instrument. This is especially important if calibration data from several instruments is to be averaged to form one calibration curve. Although each instrument can be adjusted to a standard sensitivity, readings over a range of concentrations will depend on the shape of the response curve. For both OVA's and HNU's, results on several instruments showed that if the sensitivity of each instrument is adjusted using a primary calibrant substance, subsequent measurements will have a relative precision of 8-12%. These experiments were performed on seven priority list substances using six OVA's and six HNU's. Primary calibrations and measurements were performed on the same day.

The OVA may be operated in either the "survey" mode, if the spill situation involves only one volatile organic, or the gas chromatography (GC) mode if more than one substance is involved. This capability would be useful as a screening procedure to verify that one main component is present prior to quantitative analysis using the "survey" mode. A study of the GC mode was carried out to ascertain its usefulness for spill site applications. Two OVA's were equipped with Portable Isothermal Packs (PIPS) (Foxboro Company) which maintained isothermal conditions at either 0°C or 40°C. Three different types of GC columns (manufactured by Foxboro Company) packed with 3% diisodecyl phthalate on Anakrom A, AW, 60/80 mesh (B), 10% OV-101 on Anakrom Q, 60/80 mesh (G) or 10% 1,2,3 Tris (2-cyanoethoxy) propane on Anakrom C22A, AW, 60/80 mesh (T) can be used with this system. Mixtures of 5 or 7 selected chemicals, at several

concentrations in air, were analysed on two different types of GC columns (T and G) at 0°C. Retention times were approximately 60-80% of those previously reported by the manufacturer (5). For compounds which have retention times less than 1 minute, under these conditions, the peaks are not clearly defined on the recorder chart, on which four pen marks/second are made. For compounds which have retention times greater than eight minutes, the peaks may be too broad for accurate determination of retention times. Our retention times, and those supplied by the manufacturer (5), indicate that only a fraction of the priority list compounds fall within the optimum range on any of the three columns. Thus, while the OVA's GC mode may be used to determine the presence or absence of multiple components, it will usually not be useful for identification and quantitation of the components. Table (3) compares our retention times with those reported by the manufacturer (5).

With most of the compounds studied, stable readings on both instruments were reached after a few seconds. For some high boiling point compounds, however, several minutes were needed for a stable, maximum reading to be attained. This effect should be considered when developing procedures for spill site measurements.

Response calibration data for a total of 51 substances on the OVA and 39 substances on the HNU were obtained during this study. The vast majority of these are pure compounds although a few are mixtures which are produced for commercial use. Table (1) lists all priority list substances for which data were obtained. Once the experimental study was completed, it was necessary to process the data into a form suitable for field use. In doing this, decisions were made in consultation with EETD as to the field methodology.

Data processing was carried out on a DEC PRO-350 and an IBM PC using the RS/1 and Lotus 1-2-3 software packages respectively. All data on priority list substances were corrected to a standard instrument sensitivity. This involves multiplying all readings by a factor such that the primary calibrant standard becomes equal to its concentration. This procedure is valid only if the instrument response to any chemical is proportional to the instrument response to the primary calibrant substance. This was verified for both OVA and HNU instruments using data for several priority list substances. Typical results are shown in Figure (3) for acetone. In this case, instrument response for the two substances are linearly related, even at high acetone concentrations where instrument response as a function of concentration is non-linear.

In the next step, each set of readings was averaged to produce a set of readings vs. concentrations based on the response of several instruments. Several curve fitting procedures were tried before deciding on the following functions:

OVA	x1, x10 ranges	$R = a_1 \times C + b_1$
	x100 range	$R = a_2 \times C + b_2$
HNU	all ranges together	$R = a_3 + b_3 \times (1 - \exp(-C/c_3))$
		or* $R = a_4 \times C + b_4$

Where R = instrument reading C = concentration in ppm

$a_1, b_1, a_2, b_2, a_3, b_3, c_3, a_4, b_4$ are fitting parameters

* choice of fitting function based on visual inspection of data

Figures (4) and (5) show the OVA and HNU fitted curves for acetone. Statistical analysis was done for all curve fittings. In all cases, excellent correlations were achieved as shown by the following regression coefficients:

Regression coefficient (r):	average for all substances	<u>OVA</u>	<u>HNU</u>
		.9983	.9987

In adapting the fitted data for field use, a strategy for making spill site measurements was first worked out. This was done in consultation with EETD. The goal was to maximize the ease with which readings could be taken under field conditions without loss of accuracy. The strategy is based on the following points:

1) OVA and HNU instruments will be maintained and adjusted to the standard sensitivities using the primary calibrant substances at the location from which they will be deployed to a spill site.

2) Each instrument will be supplied with a set of transparent meter scale overlays, one for each priority list substance. These overlays will be easily fitted and removed.

3) No sensitivity adjustments will be needed at the spill site. Once the identity of the spilled substance is known, the appropriate overlay can be fitted in a matter of seconds. The overlays will give direct readings of the concentration in air in ppm.

Meter scale overlays have been designed for both the OVA and HNU using the values of derived fitting parameters. This involved generating smoothed data (instrument reading vs. concentration) and converting instrument reading into angle measured from the zero line on each scale. In generating smoothed data, our objective was to produce a meter scale which has a reasonable number of marks (8-16) corresponding to a set of evenly spaced, easy-to-read concentrations. Because of the differences in instrument sensitivity and concentration range studied for each substance, the acceptable sets of concentrations used in deriving the meter scale spacings were obtained by trial-and-error calculations. This procedure was greatly facilitated by using a spreadsheet program relating concentration, reading and angle of deflection. This allowed recalculating with a new set of concentrations within a few seconds. EETD is finalizing the design for the overlays, including an easy method for fitting and removing the overlays in the field (4). Production of the meter scale overlays for field use should be completed in the near future. Figure (6) shows the OVA and HNU meter scale overlay designs for a priority list substance.

Field manuals which should be short, easily read, and geared to using the meter scale overlays have been drafted for both instruments and are being finalized in conjunction with EETD.

HACH DR-EL/4 DEVELOPMENT

Literature survey and experimental work is being done to develop quantitative methods for priority list organic chemicals which are suitable for addition to

the Hach Kit. i.e.:

1) They should make use of the instruments and if possible, some reagents already present in the Hach Kit.

2) The complexity of the procedures and training required to utilize them should be comparable to the present Hach Kit methodology.

Initially, the literature survey sought methods for the first fifty chemicals on the EETD priority list. Literature sources included published methods for quantitative analysis of water as well as qualitative or "spot tests" which normally are used to detect the presence or absence of a chemical. Next, the 150 priority list chemicals were arranged into groups, each of which could be amenable to analysis by a single method. Of particular interest are the spot tests in which the development of a coloured product, denotes the presence of a given class of compound. Our experimental evaluation addresses the aspects of stability, interferences, and the relationship between colour intensity and analyte concentration, i.e. the calibration curve. The shape of this curve determines sensitivity and detection limit. Figure (7) shows results for the m-dinitrobenzene/alkali spot test for ketones (using acetone as the analyte). The results indicate an almost linear, fairly reproducible relationship between reading and concentration over a wide range. Experimental work is planned for later this year in which sampling and extraction methods for soil and environmental water samples will be investigated. The effects of naturally occurring interferences will be evaluated as part of this study.

WORK IN PROGRESS AND FUTURE DEVELOPMENT

Developmental work on the Hach DR-EL/4 work is continuing. Several methods for priority list organic chemicals are being evaluated and will possibly be adapted for use with the commercially available Hach Kit.

The OVA and HNU instruments have been on the market for a number of years and have proved themselves to be valuable in many situations. The EETD development program is producing a set of meter scale overlays, methodologies and documentations which should enhance their use in spill response situations.

As more sophisticated instruments satisfying the Level II criteria become available, we expect that development programs, similar to the one described here, will be useful in adapting these instruments to spill response. Thus, the opportunity exists for continued improvement in spill response analytical capability.

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TABLE (1)

EETD PRIORITY LIST CHEMICALS CALIBRATION STUDIES

From the First 50 Priority List Chemicals

<u>OVA</u>	<u>HNU</u>
Acetic Acid	Acetic Acid
Acetic Anhydride	Acetic Anhydride
Benzene	Ammonia
Butyraldehyde	Benzene
Cyclohexane	Butyraldehyde
Ethylbenzene	Cyclohexane
Ethylene	Ethylbenzene
Ethylene Oxide	Morpholine
Formaldehyde (37% in methanol)	Propylene
Methanol	Propylene Oxide
Morpholine	Styrene
Propylene	Toluene
Propylene Oxide	Vinyl Chloride
Styrene	2-Ethylhexanol
Toluene	
Vinyl Chloride	
Xylene	
1,2-Dichloroethane	
2-Ethylhexanol	

From the Remaining Priority List Chemicals

<u>OVA</u>	<u>HNU</u>
Acetone	Acetone
Acetylene	Butanol
Acrylonitrile	Butylene
Butanol	Carbon Disulfide
Butylene	Dichlorobenzene
Carbon Tetrachloride	Dimethyl Ether
Chloroform	Ethanol
Dichlorobenzene	Ethylene Dibromide
Dimethyl Ether	Isopropanol
Ethanol	Methyl Ethyl Ketone
Fluorochloromethanes	Methyl Isobutyl Ketone
Isopropanol	Methyl Methacrylate
Methyl Ethyl Ketone	Methylamines
Methyl Isobutyl Ketone	Methylene Chloride
Methyl Methacrylate	n-Hexane
Methylamines	Propylene Glycol
Methylene Chloride	Turpentine
n-Hexane	Vinyl Acetate
Propylene Glycol	1,3-Butadiene
Turpentine	
Vinyl Acetate	
1,1,1-Trichloroethane	
1,3-Butadiene	

TABLE (2)

OVA TEMPERATURE STUDY

<u>Sample</u>	<u>Temperature (°C)</u>	<u>Instrument Response</u>	
		<u>Average</u>	<u>Std. Dev.</u>
101 ppm Benzene	3.5	172	35
	15.5	149	25
	24	148	18
	27	140	18
	32	124	16
93 ppm Methane	3.5	99	3
	15.5	98	5
	24	94	4
	27	90	4
	32	88	2

HNU TEMPERATURE STUDY

<u>Sample</u>	<u>Temperature (°C)</u>	<u>Instrument Response</u>	
		<u>Average</u>	<u>Std. Dev.</u>
10 ppm Benzene	3.5	18	2
	15.5	17	2
	32	17	1
101 ppm Benzene	3.5	98	55
	15.5	145	13
	32	147	7

TABLE (3)

OVA GC MODE - Retention times on a 10% 1,2,3 Tris-(2-cyanoethoxy) propane on Anakrom C22A, AW, 60/80 mesh column at 0°C

Retention Times (minutes)

<u>Compound</u>	<u>10 ppm</u>	<u>30 ppm</u>	<u>100 ppm</u>	<u>Average</u>	<u>Literature Values (5)</u>	<u>Literature Values (5)</u>
Dichloromethane	0.83	0.85	0.74	0.81	1.13	71
Benzene	1.45	1.47	1.35	1.42	1.72	83
Methyl Ethyl Ketone	2.6	2.73	2.46	2.60	3.50	74
Toluene	3.35	3.45	3.2	3.33	4.50	74
Methyl Isobutyl Ketone	6.57	6.84	6.26	6.56	7.50	87

OVA GC MODE - Retention times on a 10% OV-101 on Anakrom Q, 60/80 mesh column at 0°C

Retention Times (minutes)

<u>Compound</u>	<u>10 ppm</u>	<u>30 ppm</u>	<u>100 ppm</u>	<u>Average</u>	<u>Literature Values (5)</u>	<u>Literature Values (5)</u>
Dichloromethane	0.31	0.32	0.24	0.29	0.48	60
Benzene	0.91	-	0.83	0.87	1.32	66
Methyl Ethyl Ketone	-	0.59	0.44	0.52	0.83	63
Toluene	2.79	2.83	2.48	2.70	4.08	66
Methyl Isobutyl Ketone	2.16	2.27	1.95	2.13	3.25	65

FIGURE 1
OVA RESPONSE CURVES
ACETONE

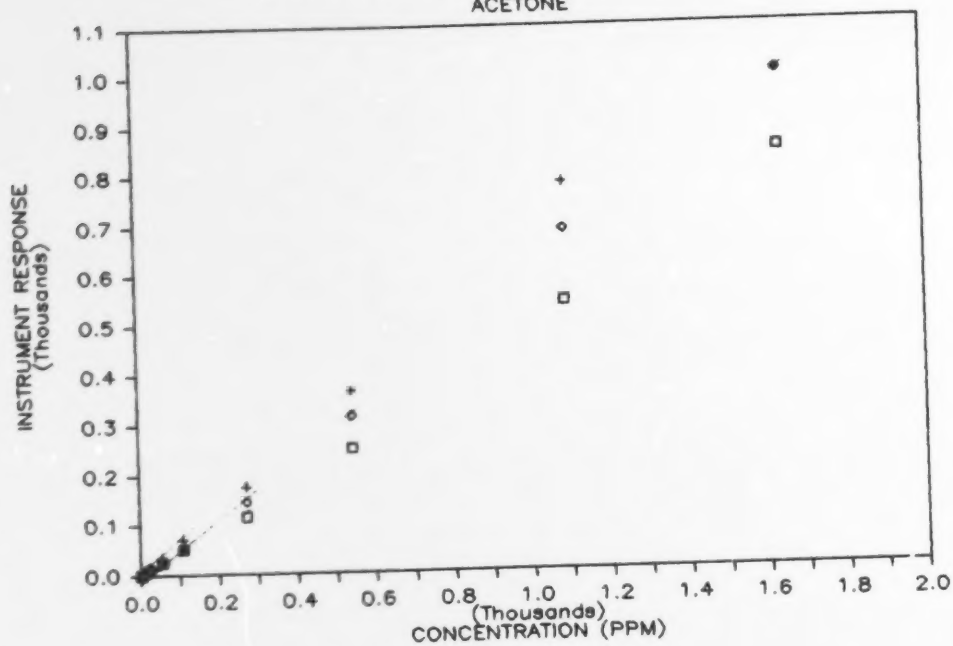


FIGURE 2
HNU RESPONSE CURVES
ACETONE

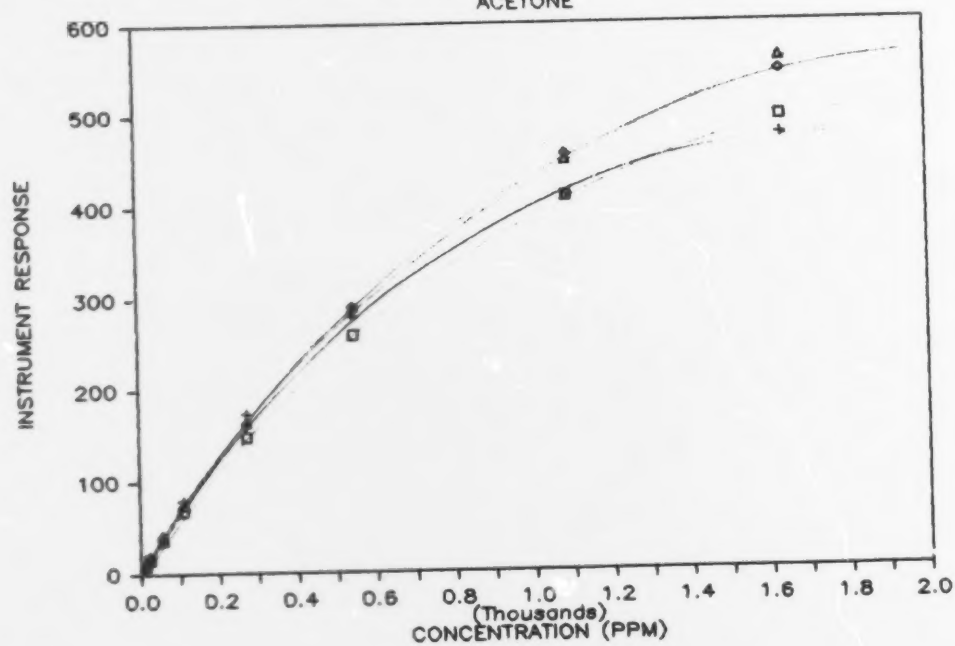


FIGURE 3
HNU SENSITIVITY STUDY
ACETONE VS BENZENE

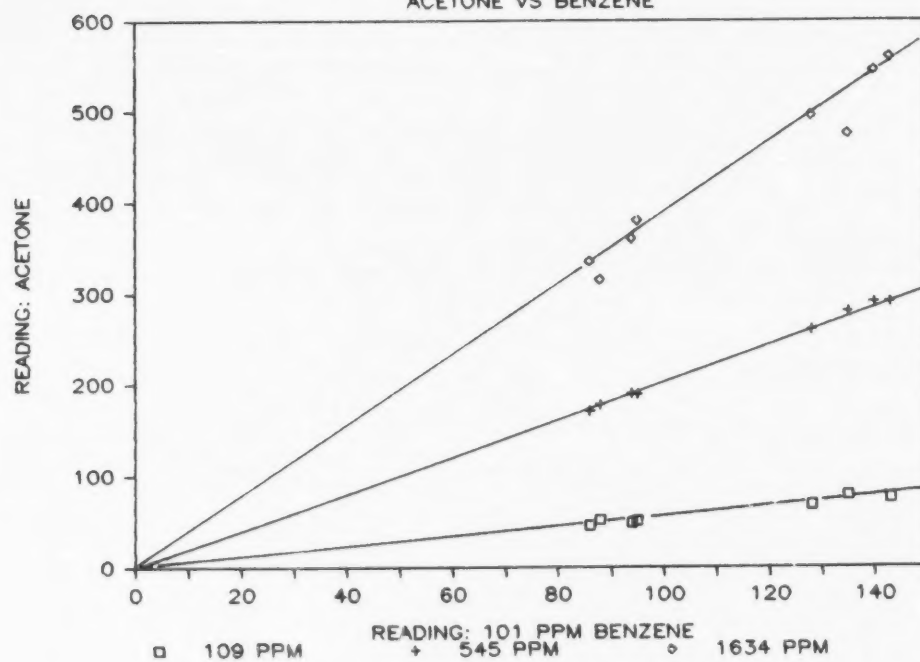


FIGURE 4
OVA CURVE FITTING
ACETONE

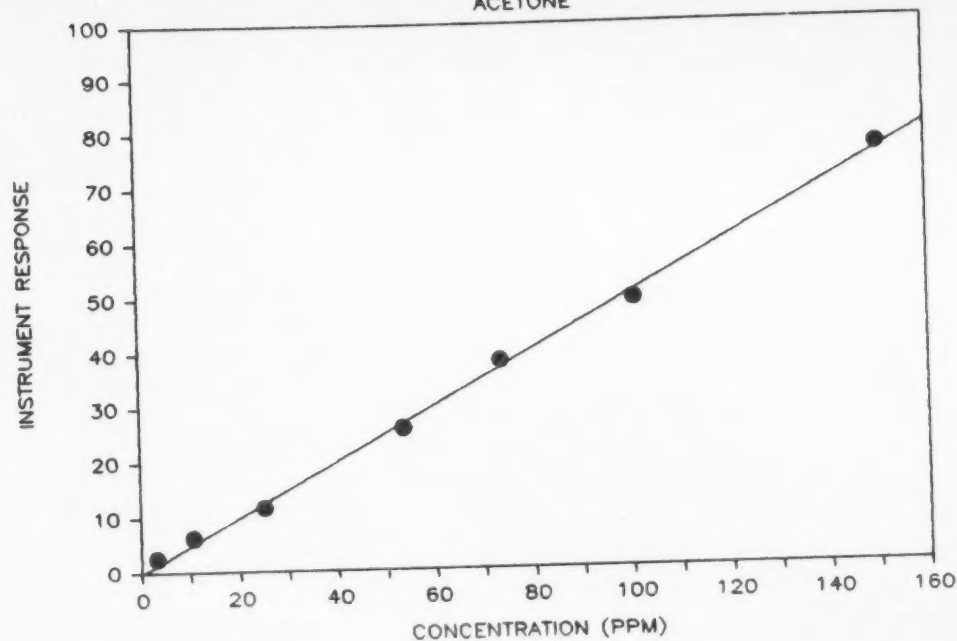


FIGURE 5
HNU CURVE FITTING
ACETONE

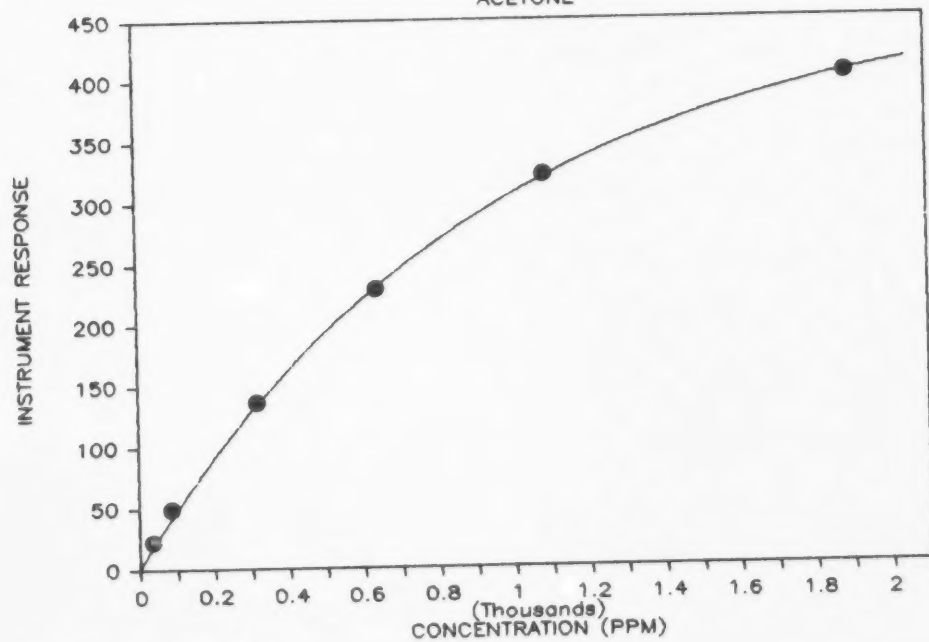
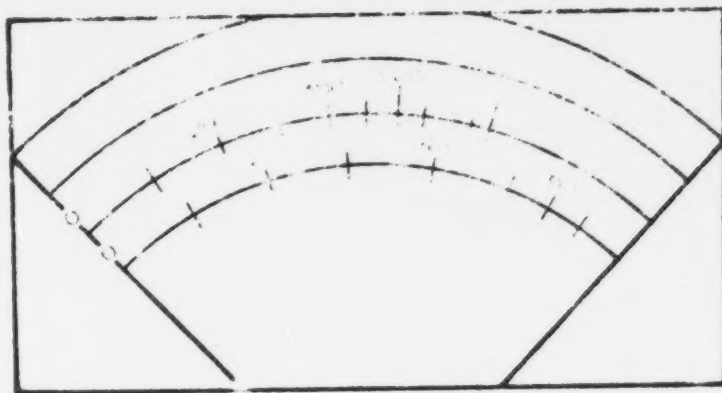


FIGURE 6
METER SCALE OVERLAY --HNU

DIBROMOETHANE — TLV = 20 ppm (1978)
IDLH =



METER SCALE OVERLAY--OVA

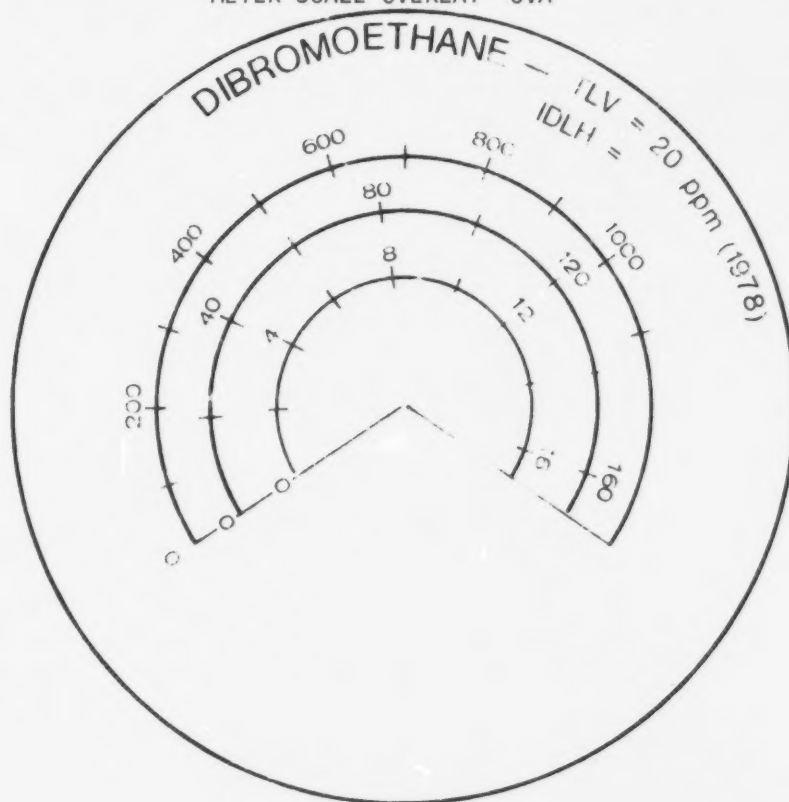
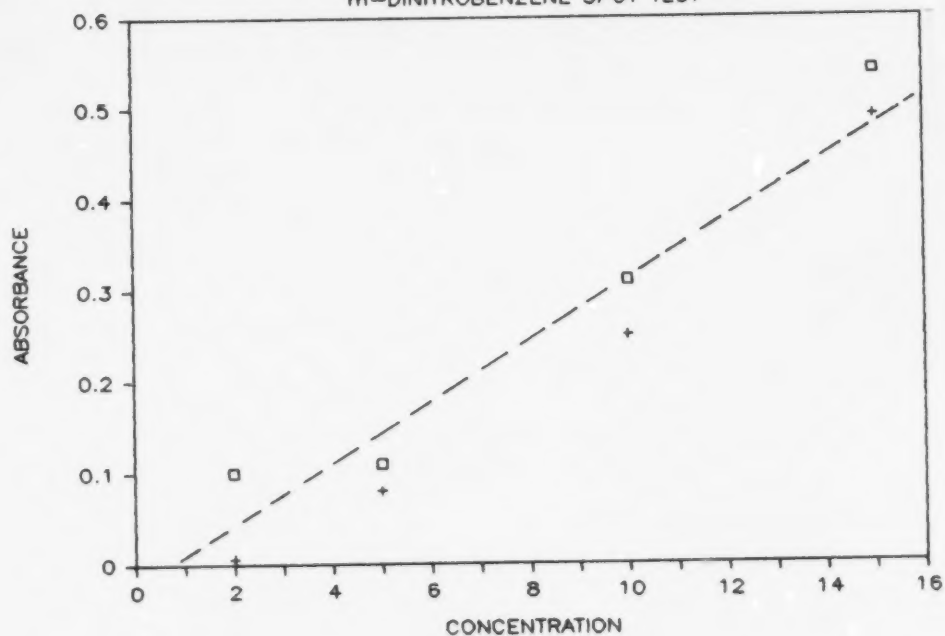


FIGURE 7
CALIBRATION CURVE — KETONES
m-DINITROBENZENE SPOT TEST



SCREENING ON-SITE AIR MONITORING SAMPLES
BY USE OF
FIELD FLAME IONIZATION DETECTION/
PHOTOIONIZATION DETECTION GAS CHROMATOGRAPH

by

Rodney D. Turpin
U.S. Environmental Protection Agency
Environmental Response Team
Edison, New Jersey

and

Phil Campagna
Ecology and Environment, Inc.
Buffalo, New York

INTRODUCTION

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to Federal On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters/Regional Offices, and other governmental agencies in the area of environmental emergencies such as chemical spills and uncontrolled hazardous waste sites.

The objectives of this paper are to briefly describe the ERT's Five Step Air Monitoring Guides, and to describe the methods/techniques used by ERT to screen air samples on-site to reduce the number of off-site samples for analysis. These objectives are obtained by describing site assessment; Field Flame Ionization Detection (FID)/ Photoionization Detection (PID) Gas Chromatograph; thermal desorption tubes; air sampling bag; and other field collection techniques.

ERT's 5-STEP AIR MONITORING GUIDES

This procedure is generally applicable to most chemical spills and hazardous waste site responses. However, since each incident is unique, modifications may be necessary. The sequence for monitoring organic gases and vapors consists of five general steps:

- Step 1 - Determine total unknown organic background concentrations.
- Step 2 - Determine total unknown organic concentration on-site.
- Step 3 - Collect on-site area air samples.
- Step 4 - Identify specific airborne contaminants.
- Step 5 - Identify particulate airborne contaminants.

1. Total Unknown Organic Background Concentrations

Background readings of total organic gases and vapors, using FID's/PID's Direct Reading Instruments (DRI), are made upwind of the site in areas not expected to contain air contaminants. If industries, highways, or other potential sources contribute to concentrations on-site, these contributions should be determined. Depending on the situation and the time available, additional monitoring should be done nearby to determine if contaminants are leaving the site.

2. Total Unknown Organic Concentrations On-site

The on-site area is monitored (using DRI's) for total gas/vapor concentrations, measured at both ground and breathing zone levels. The initial on-site walk-throughs are to determine general ambient concentrations and to locate higher than ambient concentrations (hot-spots). Transient contributors on-site, e.g., exhausts from engines should be avoided. Concentrations are recorded and plotted on a site map. Additional DRI monitoring is then done to thoroughly define any hot spots located during the survey.

3. On-site Area Air Samples

Sampling stations are located both on and off-site. The number and locations depend on evaluating many factors, including hot spots (by DRI), active work areas, potentials for high concentrations, and wind direction. As a minimum, stations should be located in a clean off-site area (control or background station), exclusion zone, and downwind of the site. As data are accumulated, location, number of stations, and frequency of sampling can be adjusted.

Routinely, two 4-hour samples are collected - in the morning and afternoon respectively - using personal sampling pumps equipped with Tenax and/or carbon-packed, metal adsorption tubes. Total gas/vapor concentration (using DRI) should also be determined at the start and finish of each sampling run. The readings obtained may show an approximate relationship (depending on organics present) which will be helpful later in placing samplers.

Samples are desorbed with a thermal desorber and analyzed on the OVA-GC for total organic concentration and number of peaks. Chromatograms of samples taken at the same location but at different times or from different stations can be compared. Differences in heights of "total" peak, number of independent peaks, and relative peak heights, if judiciously interpreted, are useful for making preliminary judgments concerning air contaminant problems.

If relatively high concentrations are detected by the initial DRI surveys, samplers equipped with carbon-packed collection tubes (glass) are run next to Tenax/carbon-packed, metal equipped samplers. The latter samples are analyzed in the field. The carbon-packed collection tubes are analyzed by a American Industrial Hygiene Association (AIHA) accredited laboratory.

Area surveys using DRI are continued routinely two-four times daily. These surveys are to monitor for general ambient levels, as well as levels at sampling stations, hot-spots, and other areas of site activities. As information is accumulated on airborne organics, the frequency of surveys can be adjusted.

4. Specific Airborne Contaminants

Personal monitoring pumps with carbon-packed collection tubes (glass) are run on the first afternoon, concurrent with samplers equipped with Tenax/carbon-packed, metal collection tubes. Generally, when total gas/vapor readings are low and only a few peaks seen (from the field GC analysis of morning samples), 100-150 mg carbon-packed tubes (glass) are used and operated at a flow rate of 100 cubic centimeters/minute until approximately 30 liters of air have been collected. Depending on unsuspected contaminants and their concentrations, higher flow rates and/or volumes may be needed. When total gas/vapor readings are high and there are many peaks (from the morning samples), then larger glass carbon collection tubes (600 mg) are operated at a flow rate from 0.5 to 1 liters/minute to collect 90 to 150 liters of air.

The results from laboratory analysis of glass carbon tubes are used for a number of different purposes, including:

- ° To identify and measure organic gases and vapors collected during the sampling period.
- ° To compare laboratory chromatograms and field chromatograms. If only a few peaks (but the same number) are seen on each chromatogram (and identified on the laboratory chromatogram) from samples collected at the same location, it may be reasonable to assume, until standards are run on the field GC, that the two chromatograms are identifying the same materials.
- ° To identify major contaminants on laboratory chromatograms and determine what standards to prepare for the field GC. Field GC's can then be used to identify and measure air contaminants against laboratory prepared standards.
- ° To use the field GC as a screening device for determining when samples should be collected for laboratory analysis, or when samples previously collected should be analyzed. Changes in the number of peaks on the field chromatograms from samples collected at the sample location indicate changes in the air, suggesting the need for collecting additional samples for laboratory analysis.

If desorption equipment is not available for on-site sample analysis, glass collection tubes should be collected daily. Only samples collected every third to fifth day are sent to AIHA accredited laboratories for analysis; the remaining samples are stored in a cool place (preferably refrigerated).

Selected stored samples are analyzed if third to fifth day samples indicate changes in air contaminant patterns. If daily on-site surveys detect low contaminant(s) levels, then 100-150 mg glass carbon columns are used. If the survey reveals relatively high levels of contaminants, then 600 mg glass carbon tubes are used.

The National Institute for Occupational Safety and Health P&CAM Analytical Method NO. 127 should be followed as closely as possible. Flow rates and collection tubes described in this guide are primarily for organic solvents. If other than organic solvents are suspected, then the NIOSH Manual of Analytical Methods (Volume 1-7) should be consulted for the appropriate collection media and flow rates.

Particulates and Aerosols

Sampling for particulates is not done routinely. If these types of air contaminants are known or suspected to exist, a sampling program is instituted for them. Incidents where these contaminants might be present are: fires involving pesticides or chemicals, incidents involving heavy metals, arsenic, or cyanide compounds, or mitigation operations that create dust (from contaminated soil and excavation of contaminated soil).

Sampling media and analytical methods for these air contaminants should follow guidance given in the NIOSH Manual of Analytical Methods. Field portable Real-time Aerosol Monitors can be useful in determining the amount of particulates above background if any are present.

COLLECTION MEDIA AND FLOW RATES

The major problems with trying to select collection media(s) for hazardous waste site or chemical spill responses are the number of potential unknown and/or uncontrollable factors. These unknown factors include (but are not limited to) the: (1) type of contaminant (organic/inorganic); (2) physical state of air contaminant (vapor, gas, aerosol, etc.); (3) atmospheric conditions (wind, rain, temperature, etc.); (4) site condition(s) (stable/unstable); (5) geographic conditions (valley, mountain, coastal, etc.).

When time, budget, and site conditions warrant, the ERT prefers to run a variety of collection medias at different flow rates. Both carbon spheres and Tenax thermal desorption tubes provide some important information if analyzed on-site with a field GC even if standards are not available.

The on-site analysis is Step No. 3 previously mentioned and provides both collection media as well as rate information. This data furnishes the total concentration and number of organic contaminants present at the select flow rate(s) if analyzed on an OVA. Although identification of airborne contaminants is premature at this point, data received may indicate the appropriate flow rate for carbon and/or Tenax collection media. In addition, the on-site data indicates which (if any) of the sample stations has the

highest potential for organic contaminants. This can be obtained by observing both the total concentration and the total number of gas chromatograph peaks per sample.

Based on the data mentioned in Step No. 3, as well as site assessments, ERT has found it useful to use the following media for Step No. 4 of the ERT Air Monitoring Guides: florosil, carbon, silica gel as well as ERT 2-state Tenax/chromosorb GC/MS thermal desorption tube. This approach assists in determining the appropriate collection material for any additional sampling which may be necessary at a later date.

FID/PID SAMPLE SCREENING

Once airborne contaminants have been identified by off-site GC analysis and confirmed by GC/MS analysis, the authors have been able to screen future samples for analysis by using a field FID/PID GC with appropriate standard using either carbon sphere and or Tenax thermal desorption tubes.

FIELD ANALYSIS PROCEDURES

The following procedures are used by ERT to perform field analysis of air samples collected at uncontrolled hazardous waste site/chemical spills using the Century OVA and/or the Photovac GC with the Century Program Thermal Desorber (PTD).

The carbon sphere and/or Tenax sorbent collection tubes used for sampling are cleaned by desorbing the tubes three times using the PTD at a temperature of 225°C and desorption rate of 60 ml/min. The predesorbed tubes are then placed in a sealed jar and allowed to cool to room temperature.

The tubes are then connected to personal air sampling pumps and calibrated to a specific flow rate (e.g., 50 cc/min to 500 cc/min) using a precalibrated rotometer. The pumps are then placed at sampling locations on-site, as well as downwind and upwind of the site. Pumps are allowed to run from 2-8 hours depending on the levels of contamination.

The sorbent collection tubes are placed into the PTD once the oven has reached the desorption temperature (usually 250°C). Tubes are desorbed at a rate of 60 ml/min into the PTD's collection chamber while connected to the Century OVA. If the Photovac GC, in addition to the OVA, is being used with the PTD, a PTD "T" septum adaptor filter is placed on the sample outfitting of the PTD instead of directly connecting it to the OVA. The open end of the "T" fitting is then connected to the OVA.

After the desorb cycles have been completed, the "read" button is engaged. This allows the OVA to pull a portion of the sample in the PTD into the OVA. The reading appearing on the strip chart recorder and OVA readout probe is the total organic vapors collected on the tube in ppm as methane. This total value will be used to calculate the time weight average for the sample,

and also in determining what attenuation setting the GC will be run at for the OVA and Photovac. It will also assist in determining the injection volume that will be used on the Photovac. Because of the sensitivity of the Photovac, a large sample injection may cause poisoning of its detection.

After the total reading has been taken, the "read" button on the PTD is again engaged. As the reading on OVA probe reaches the maximum constant value, the inject value of the OVA is engaged and this starts the GC run for the OVA. Also at this point, a sample is drawn using a gas tight syringe from the "T" septum fitting for the Photovac GC. This sample is then injected into the Photovac GC for its run. The GC run for the OVA is usually 20 minutes for unknown compounds - 10-15 minutes when using the Photovac GC.

After the analysis has been completed, the GC column on the OVA and Photovac GC are backflushed for approximately 1 1/2 times the chromatographic run time. During this period, the PTD and sorbent are cleaned 5 times by purging. The last purge is done without the sorbent tube in the PTD; this allows for cleaning of the PTD chamber and sampling lines. The procedure is followed until all samples have been analyzed. It should be noted that before the first sample is analyzed, a system blank and a sorbent collector tube blank are analyzed. This allows for the determination of ghost peaks which may be due to contaminants.

The standards are made up in either air bags or gas cylinders by an outside lab and usually consist of the major constituent that have been previously identified by either standard NIOSH methods and/or GC/MS.

After all samples and standards have been analyzed, the information is used to assist personnel on-site to determine which samples, if any, require off-site laboratory analysis. Also, during long term cleanup operation when standards are used, this information assists the On-Scene Coordinators in determining if site conditions are changing and whether operations are causing release of new or greater quantities of organic vapors.

CONCLUSIONS

The authors hope other field response individuals find this summary of the ERT 5-Step Air Monitoring Guides and discussion of their FID/PID on-site screening technique useful. The procedures mentioned are currently being used by ERT and others at both hazardous waste sites and chemical spill responses. The procedures are continuously being updated and modified for each specific response.

ACKNOWLEDGMENT

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DEVELOPMENT OF A VEHICLE-PORTABLE ANALYTICAL
SYSTEM FOR CHEMICAL EMERGENCIES

A.M. Bobra
Environment Canada
Environmental Emergencies Technology Division
Ottawa, Ontario

INTRODUCTION

A number of chemical spill accidents in Canada have demonstrated the need for systems to rapidly determine quantitatively and qualitatively, the spilt materials in air, water and soil. As part of the focus on dealing with chemical spills, the Environmental Emergencies Technology Division (EETD) of Environment Canada addressed this problem of rapid analytical techniques suitable to spill situations in Canada. In 1980, a review of the literature was commissioned which concluded that systems directly usable for spill responses did not exist. A number of systems were identified which had the possibility of being evaluated and developed for this purpose.

The existing capability was divided into five levels, based on criteria of portability, accuracy and complexity. The levels were:

- Level 1 Pocket-portable systems based on visual changes in prepared chemical tubes (e.g. Dräger tubes);
- Level 2 Person-portable systems based on electronic detectors (meters);
- Level 3 Vehicle-portable (small van) systems based on computer-controlled instruments with pre-developed software;
- Level 4 Mobile laboratories (towable on good roads); and
- Level 5 Fixed laboratories (not portable).

To focus the development of these analytical capabilities on appropriate targets a priority list of 150 chemicals was also developed by EETD (1982) (1), based on spill frequency and spill consequences. The chemicals on the list accounted for greater than 90 percent of chemical spills and spill volume in Canada. EETD research on the various levels of analytical capability was geared to the chemicals on the list.

Level 3 was considered to be the most appropriate for quantitatively and qualitatively monitoring substances in all three environmental compartments following a spill. With this information, EETD proceeded with the task of improving the state-of-art of this technology.

In this paper a brief review of the concepts and the EETD research programs on the development of Level 3 is presented. The programs had been contracted to Farrington, Lockwood Company Limited in 1983 and to Underdown Chemometrics Limited in 1984. Introduction work on the development was presented at the 1983 Technical Seminar on Chemical Spills by Lockwood and Halman (2).

LEVEL 3 CONCEPT

The Level 3 concept involves instrumentation which would normally be found in a fixed laboratory and operated by a trained operator. The instrumentation would be located in a small van, containing some support equipment, electrical power and a suitable climate for operation. The equipment would make use of available microprocessor technology in the form of a dedicated microprocessor

and/or accompanying microcomputer. A primary function of the associated software is to make it possible for a person with little chemical training to operate the instrument and obtain results useful for spill response. This would be accomplished by providing a user-friendly interface during the data acquisition and analysis steps, and by performing certain control and analysis tasks normally done by an operator with chemical training.

Level 3 instrumentation would not be as easily transportable as those belonging to Level 1 and 2, and may require greater operator skill. However, it would have greater inherent accuracy and the capability to handle samples containing more than one detectable substance. It is anticipated that Level 3 capability would be needed at spills of highly toxic substances, at spills of more than one substance and in situations where samples of complex media (e.g. soils) are involved.

DEVELOPMENT OF LEVEL 3

After having developed Level 3 concepts, EETD proceeded to assess the potential application of commercially available analytical instrumentation. Three microprocessor-based systems were selected by EETD for development as Level 3 systems. The systems consisted of:

- I Gas chromatography (GC)
- II Infrared spectroscopy (IR)
- III Ultraviolet and visible spectroscopy (UV/VIS)

It was anticipated that the spectrophotometers' main Level 3 role would be that of substance identification while the GC would be the primary instrument for obtaining quantitative analytical results.

Gas Chromatography

Developmental work on Level 3 analytical systems has concentrated primarily on this system. A Perkin-Elmer Sigma 2000 Gas Chromatograph with a microcomputer-based Perkin-Elmer (PE) 3600 Data Station was selected as a Level 3 system in the EETD studies. The Sigma 2000 was equipped with a photoionization detector (PID) and a flame ionization detector (FID). The FID is universal detector for organic compounds and the PID is more selective for organic compounds and can also respond to several inorganic compounds. Since the PID is essentially a non-destructive detector, the effluent from this detector was directed to the FID, without splitting the stream across two detectors. The gas chromatograph was also equipped with a 1 % SP-1000/60-80 Carbowax B packed column and both standard flash evaporation and head-space analyzer sampling options. The head-space analyzer can be used for direct analysis of organic priority list chemicals in water and soil, eliminating the need for extensive sample preparation (e.g. extraction, clean-up, concentration).

The PID and FID detectors complemented the Level 2 air monitoring detector systems (e.g. HNU and OVA systems) and should be suitable for most field applications.

The Sigma 2000 GC has been interfaced to a PE 3600 Data Station. Perkin-Elmer software has been used to control data acquisition, storage and preliminary processing. The last step consisted of searching the data for peaks, computing their areas and retention times, calculating amounts present and reporting this information.

A chromatograph library system has been developed which will make analysis and identification of samples possible under Level 3 conditions. The system was designed to run on the Perkin-Elmer 3600 Data Station and was written in Microsoft BASIC. The system consisted of two programs. One was designed to produce a library of retention times and peak areas for substances on the EETD priority list. It contained the following features:

1. The program inputted data from one or several runs of a single compound, plus a standard reference sample during one session.
2. Retention times and peak areas were normalized relative to the benzene standard.
3. PID/FID peak area ratios were calculated using the individual peak areas relative to benzene.
4. Missing values were assigned a -1 value.
5. The data for the single compound were written into the library as a record having the following structure:

Compound Name	Library #	Relative PID Retention Time	Relative FID Retention Time	Relative PID/FID Peak Area	PID Response Factor	FID Response Factor
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6. This record was automatically inserted into the library on the basis of its average retention time. Thus, the library always remained ordered by increasing retention time.
7. The average retention times used in the sorting process were averages of PID and FID times, if both were available. If not, only the available one was used.

The second program was designed to perform identification and quantification on multicomponent samples using chromatography library data. The program accessed the library files created by the first program and the report file created by the Perkin-Elmer software. It contained the following features:

1. The program inputted data on multi-component samples from report files on diskette and made comparisons with the library file, which was also on diskette. The number of peaks in each file was determined automatically by the program.
2. Data for the benzene standard run during the same session as the sample was inputted from the keyboard.
3. Retention times and peak areas were converted to relative values by dividing by the corresponding value of the benzene standard.
4. The program compared the retention times of the peaks from both detectors to check for correspondence, assuming retention times within .02 minutes on different detectors belonged to the same peak.

The program produced a list of independent peaks with data entries for both the FID and PID detectors. For peaks where a FID-PID correspondence was found, data will be present for both detectors. Otherwise, peaks will have data from one detector and -1's for the other.

5. The user may choose to have all peaks on the independent peaks list analysed or may specified minimum and maximum retention times for peaks to be analysed.
6. The program performed identification for each independent peak based on average retention time to obtain four candidate substances and then ranked these candidates based on the following criteria:
 - A) if no data were missing, the error function used for ranking was a combination of relative retention time error and relative PID/FID peak area ratio error; and
 - B) if any data was missing from either the sample peak or the candidate the error function was based solely on retention times.
7. Missing values were assigned the value of -1.
8. Average relative retention times were calculated as in the first program.
9. The program will report library compounds matching a sample peak within 95 percent based on the matching criterion. A maximum of three closest matches will be reported if they are within the 95 percent criterion.
10. Quantitation was performed for each reported library compound based on relative response factors. If PID and FID data were available for both the sample peak and library compound, a value was reported which is an average of those obtained with the two detectors. Otherwise, only the available data was used.

These two programs which would automatically acquire and manipulate data to provide a list of the best fitting compounds according to the retention time and the PID/FID response ratio of the known compounds in the data base, have been debugged and tested using a very limited number of real and synthetic data. The library contained the real data of fifteen compounds. However, it was realized during the testing of the system that the Perkin-Elmer 3600 Data Station had limited integration capability and suffered from several hardware/software problems. Before the system can be made operational and suitable for field use, the system's hardware and software will have to be modified to correct the analytical problems. Only then, will the library data base for compounds in all three environmental media (direct injection (air), headspace analysis (water and soil)) be further developed.

UV/VIS and IR Spectrophotometers

The EETD selected a PE 683 IR Spectrophotometer and a PE 552 UV/VIS Spectrophotometer as Level 3 systems, to complement and supplement the GC analytical capability. The instruments were interfaced to a TRS-80 Mark III computer data analysis. Developmental work on these two systems is only in the initial stage.

The IR system appears to have the greatest application in the analysis of spill site air samples, while the UV/VIS system is expected to be the most useful for the analysis of priority substances in the water and soil matrices. These analyses are non-destructive which also allow for subsequent GC analysis of a sample if concurrent analysis is not possible or practical.

The features required for the Level 3 UV/VIS and IR computer systems are:

- 1) real-time acquisition of data from the spectrophotometer;
- 2) ability to identify contaminants by comparing sample spectra to a library of laboratory-compiled standard spectra of priority substances;
- 3) quantitation capability once the identity of the priority substance has been determined by the system; and
- 4) user-oriented computer software to allow for effective operation of the systems by operators lacking extensive technical backgrounds.

Future Development

In the future, deficiencies in the gas chromatographic analysis hardware and software are to be corrected, following this, further development of the Environmental Emergencies Technology Division's Level 3 Analytical System is to be continued in order to make it field usable for the quantitative and qualitative determination of spilt materials in air, water and soil.

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CONTAINMENT AND RECOVERY OF A CHROMIC ACID LOSS

James P. Phimister, Senior Hydrogeologist, and
Robert C. Dicken, Senior Geochemist; Gartner Lee
Associates Limited, Markham, Ontario

ABSTRACT

In December 1982, a manufacturing firm in Ontario discovered that a chrome plating tank had leaked about 5000 pounds or 1700 gallons of chromic acid beneath the floor of the plant. The lost acid was discovered seeping into a ditch near the plant.

Several test holes were augered through the floor and around the perimeter of the building to determine the extent of the spill and to provide locations for recovery well construction. Well points were used to pump chromic acid out of the ground until recovery rates declined.

A flushing system using some well points to inject water and other well points to pump from was instituted to improve recovery rates. The flushing system was used for a period of five months at the end of which time 80% of the chromic acid had been removed from the ground and recovery rates had dropped significantly. A passive collection system was left in place to collect any of the remaining chromic acid as it seeped out from under the plant.

INTRODUCTION

In early December 1982, it was discovered that a chrome plating tank located in a manufacturing plant in Southwestern Ontario had leaked its contents through a sump pit. This tank was beneath an unused chrome plating machine. About 1700 gallons of chromic acid at a concentration of around 47 ounces per gallon were lost. That is, approximately 5000 pounds of chrome leaked from the tank. The Ontario Ministry of the Environment was notified and given details of the loss.

The lost chrome was first noticed in a ditch used to carry water from a roof drain beneath the floor of the plant to a public watercourse. Chrome was discharging from the granular material around the drain pipe. The company constructed a dam across the ditch and the contaminated water was pumped into a tank. Several test holes were augered into the ground outside the plant and through the floor inside the plant to determine the extent of the chrome spread.

Perforated plastic pipe was placed in many of the augered holes so that samples could be taken on a regular basis. Several of the holes were pumped in an attempt to recover the lost chrome. In late December, 1982, Gartner Lee Associates Limited were retained by the company to carry out a containment and recovery program.

SITE GEOLOGY AND SOILS

Prior to the construction of the building where the chrome was lost, a geotechnical investigation had been carried out that included augering holes into the native soils. These holes were reported to have as much as 20 feet of overburden and bedrock was not confirmed in any hole. The stratigraphy from the geotechnical logs appeared to be about 5 feet of clayey silt at surface overlying a clayey silt till. A hard shale like clay was reportedly found below this till at depths of 10 - 13 feet. Water table was almost at ground surface at the time these holes were augered. Occasional sand seams were reported in some of the test holes. Ground elevation was about 708 feet a.s.l.

Beneath the building, about 1 foot of native soil was removed and a sand and gravel mixture, "granular B", was placed to bring the finished floor elevation to 713 feet. The bottom of the granular B is at approximately 707 feet. The tank that leaked was placed in this granular B layer (Figure 1).

The geotechnical investigation included grain size analyses on samples of the granular B and the underlying till. Using a formula that relates grain size to permeability, it was concluded that the permeability of the granular B was about 10^{-3} to 10^{-4} cm/s and the till was about 10^{-9} cm/s.

As part of monitor construction, Gartner Lee Associates Limited bored holes into the underlying bedrock. (Figure 2). A complete core was taken to check for sand seams in

the glacial till. There were no distinct sand seams but there was a minor component of sand mixed in the till matrix. The core was retained and stored for future inspection.

The bedrock is an interlayered mixture of shale and till with the odd thin limestone bed. The permeability of this formation appears to be very low judging by the grain sizes present in the till and the lack of open fractures in the shale or limestone.

GEOCHEMICAL ANALYSES

Seven soil samples were submitted for geochemical analysis in order to provide a preliminary estimate of soil chromium adsorption. Four samples were collected from the top six inches of sediment in the ditch which had received chromium contaminated water. One sample was collected from another off-site uncontaminated area to establish background conditions. In addition to these, a sample of chromium contaminated gravel from below the floor near the tank was collected and sieved into two different grain sizes.

All samples were analyzed for total chromium after acid digestion and both total and hexavalent chromium after an aqueous leach. The ditch sample analyses showed that the total (acid digestion) amount of chromium in the ditch sediments is between two and eleven times the background level. The aqueous leach results indicated that whatever chromium was present, was strongly adsorbed to the soil, and was unlikely to be leached by water.

Based on these results, it was concluded that no significant amount of chromium would be released when rainfall or runoff contacted the ditch sediments, and that excavation and off-site disposal of these soils was not necessary.

The granular B analyses showed much higher levels of total chromium (acid digestion). In addition, the aqueous leach results suggested that between 95% and 100% of this chromium was leachable with water. In other words, most of the chromium was not strongly adsorbed onto the granular B and would likely be mobile whenever the gravel was saturated with water.

The difference between the aqueous leach total and hexavalent chromium concentrations was assumed to be trivalent chromium. This suggested that between 30% and 36% of the hexavalent chromium was reduced to the less toxic trivalent form.

However, these figures were obtained on a sample of soil that was handled extensively before chemical analysis. The actual reduction of hexavalent chromium in the ground was probably considerably less.

SUMMARY OF CLEAN-UP ACTIVITIES

At the time Gartner Lee Associates Limited was retained, several initial steps had been taken to define the extent of contamination, to contain the further spread and to recover the lost chrome. A careful review of the program already in place was made prior to establishing the recovery system. Although containment and recovery

of the contaminant was of prime importance, the company wished to carry on plant operations with a minimum of interruption.

The first step in recovery was the installation of properly sized well screens and casings in selected holes so that fluids could effectively be pumped into and out of the granular B. The company used its own chemist to carry out analyses for chrome concentration in the recovered fluid and had established an excellent method of recording recovered chromic acid from the start. In addition, a water level monitoring and recording method was begun prior to pumping.

On January 8, screens were placed in several test holes and on January 9, pumping began. Figure 3 shows the water table contours as of December 23, 1982 before pumping began and Figure 4 shows the chrome concentrations before pumping. Figure 5 shows the water table contours after pumping and Figure 6 shows the chrome concentrations after pumping began. It can be seen that the water levels in the ground decreased as much as 1.5 feet while the chrome concentrations in some holes rose.

All extracted water was pumped to storage tanks where the volume and chrome concentration were measured to keep account of the total amount of chrome recovered. The hexavalent chromium was converted to trivalent chromium within the plant and existing treatment and disposal methods were used on the trivalent chrome.

During the pumping phase, the winter was exceptionally mild and rainfall caused water to infiltrate the granular B

around the perimeter of the building. After rainfall events, the chrome recovery increased in certain holes as the new water dissolved chrome on passing through the contaminated area towards the pumping wells. The water flow direction in the granular B was maintained in an inward direction from the perimeter of the building by the pumping wells. As pumping continued, a large portion of the granular B was dried up due to a decline in the water table.

In the second phase of this project, several wells around the perimeter of the building were converted from pumping wells to injection wells; water continued to be pumped from the wells inside the building. In this manner, any chrome that was mobilized by the injection water moved into the plant rather than towards the ground outside.

The injection and pumping program caused many of the originally poor producing wells to start yielding relatively high concentrations of chrome. This was due to the injection water spreading into areas where the granular B had previously been almost dry. As the water injection program continued, it became apparent that there were channels in the granular B that had a much higher permeability. Most of the recovered water and chrome was produced from wells located in these channels.

Towards the end of February, when the concentration of chrome in some holes had begun to drop, some individual holes, where production had been high, were injected with water for an hour or two at a time and then pumped. This increased the amount of chrome recovered the first few

times it was attempted. In March, water injection from the outside was continued for a 24 hour period and the granular B was filled up to the level of the bottom of the chrome plating tank. This resulted in the recovery of chrome at a relatively high rate for a short period of time.

As pumping and injection proceeded, the total amount of chrome recovered rose to about 4000 pounds (Figure 7). During initial recovery stages, the chrome concentrations in some holes was very high, in the order of 20,000 mg/L, but the volume recovered was low. As injection and pumping progressed, the concentration of chrome in the wells dropped but the recovered volumes increased substantially. Based on a calculated loss of 5000 pounds of chrome, almost 80% of the chrome was recovered. Figures 8 and 9 show the water table contours and the chrome concentration in May, 1983.

In the latter part of June, even with water being added to saturate the granular B, the amount of chrome being recovered diminished significantly. The remaining 20% of the lost chrome was dispersed through the granular B to such an extent that when water was added to saturate the material, the dilution that occurred reduced the concentrations to very low levels. In fact, if the affected volume of granular B were taken as 30,000 cubic feet (100'x50'x6') then there would be about 0.5 ounces of chrome left per cubic foot of soil in the spill area at this time. This chrome is very slowly being released as water levels in the granular B fluctuate after precipitation and is continuing to discharge where the roof drain tile leaves the building.



Barrels were placed in the granular material surrounding the roof drain tile. Water is collected from these barrels. This was the original discovery point for the chrome and has produced chrome on a regular basis from the start of clean-up. The conduit for the chrome to arrive at this point is the granular materials surrounding the drain tile beneath the floor.

Near the end of June, 1983, the active injection and pumping method of recovery was stopped and the passive recovery system, consisting of the barrels in the granular material around the roof drain tile, was left in place. These barrels slowly collect contaminated fluid seeping out from beneath the floor. When required, the barrels' contents are pumped into the plant for treatment and recovery.

To establish ground water flow directions in the bedrock and to observe the quality of water in the rock, three boreholes were drilled and monitors were constructed near the boundary of the property. These monitors were sealed with peltonite to prevent the migration of water out of the overburden or from the ground surface. A routine monitoring program including the bedrock monitors and holes through the plant floor, has been carried out since the active recovery system was shut down. The Ontario Ministry of the Environment continues to receive copies of the monitoring results.

CONCLUSIONS

Through the use of a pumping and injection program, approximately 80% of a 5000 pound chromic acid loss

was recovered within about six months. A passive collection system that has been left in place is slowly recovering any remaining chromic acid that seeps from beneath the floor.

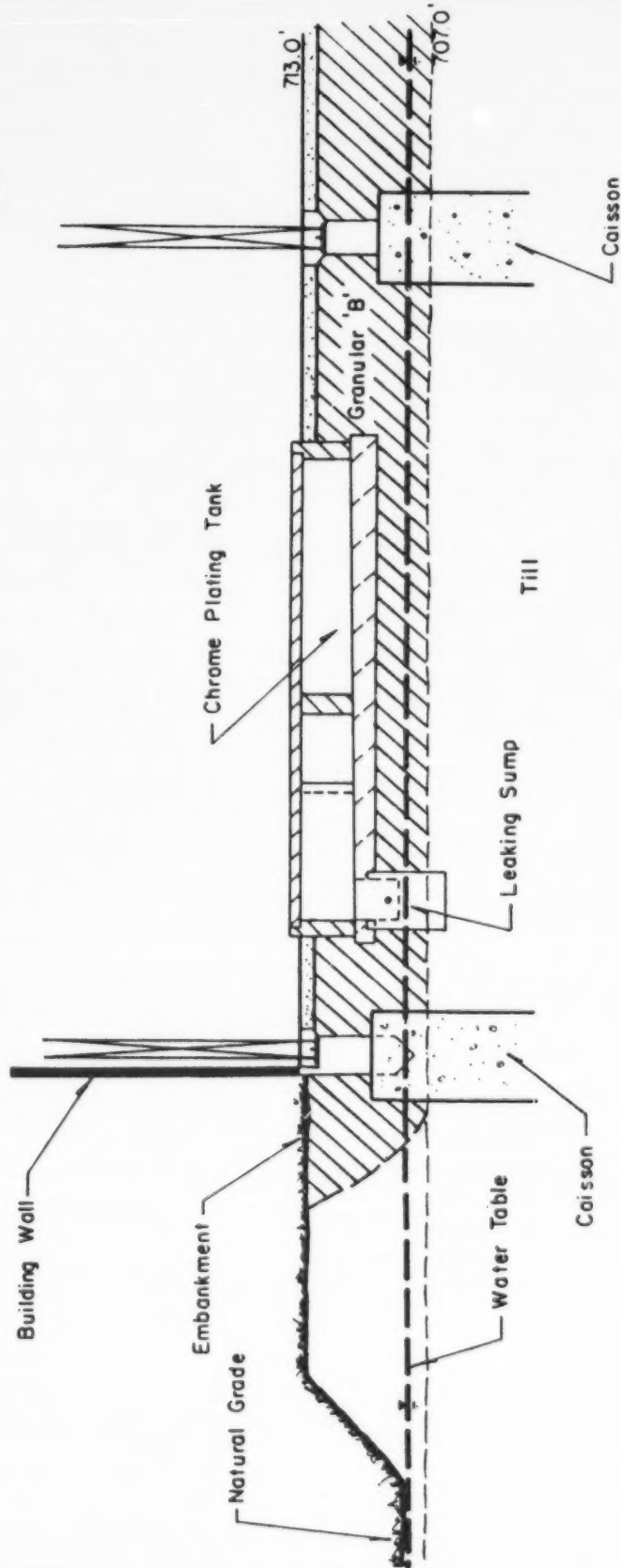
The permeability of the natural material beneath the granular B is very low and the downward gradient towards the bedrock is also extremely low. Based on the slow travel times and the amount of dilution available, it is unlikely that any chrome contamination beyond acceptable limits will occur in ground water moving off the property.



CROSS SECTION BENEATH CHROME PLATING TANK

NORTH

SOUTH



NOT TO SCALE

Typical Ground Water Monitor Installation

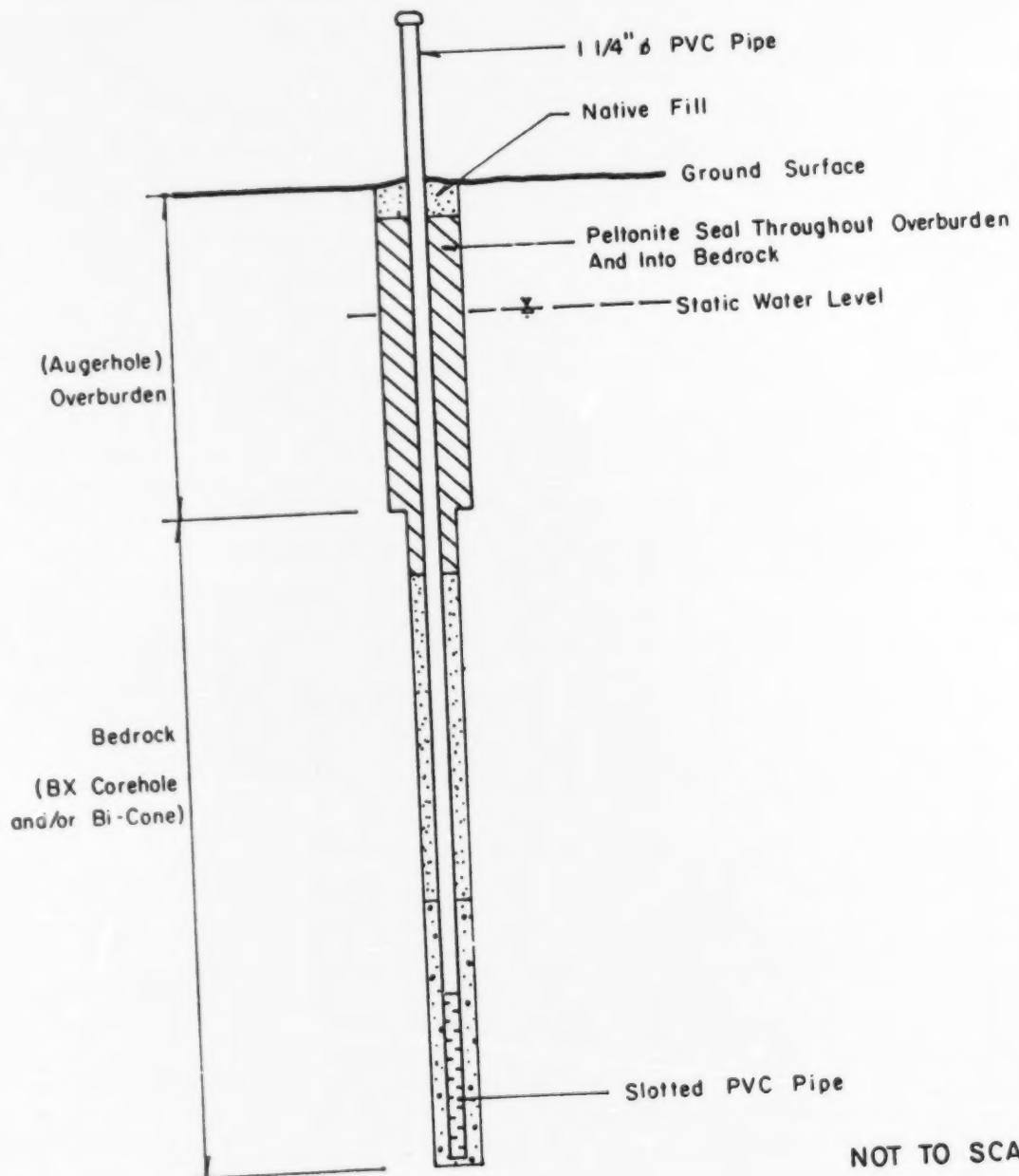
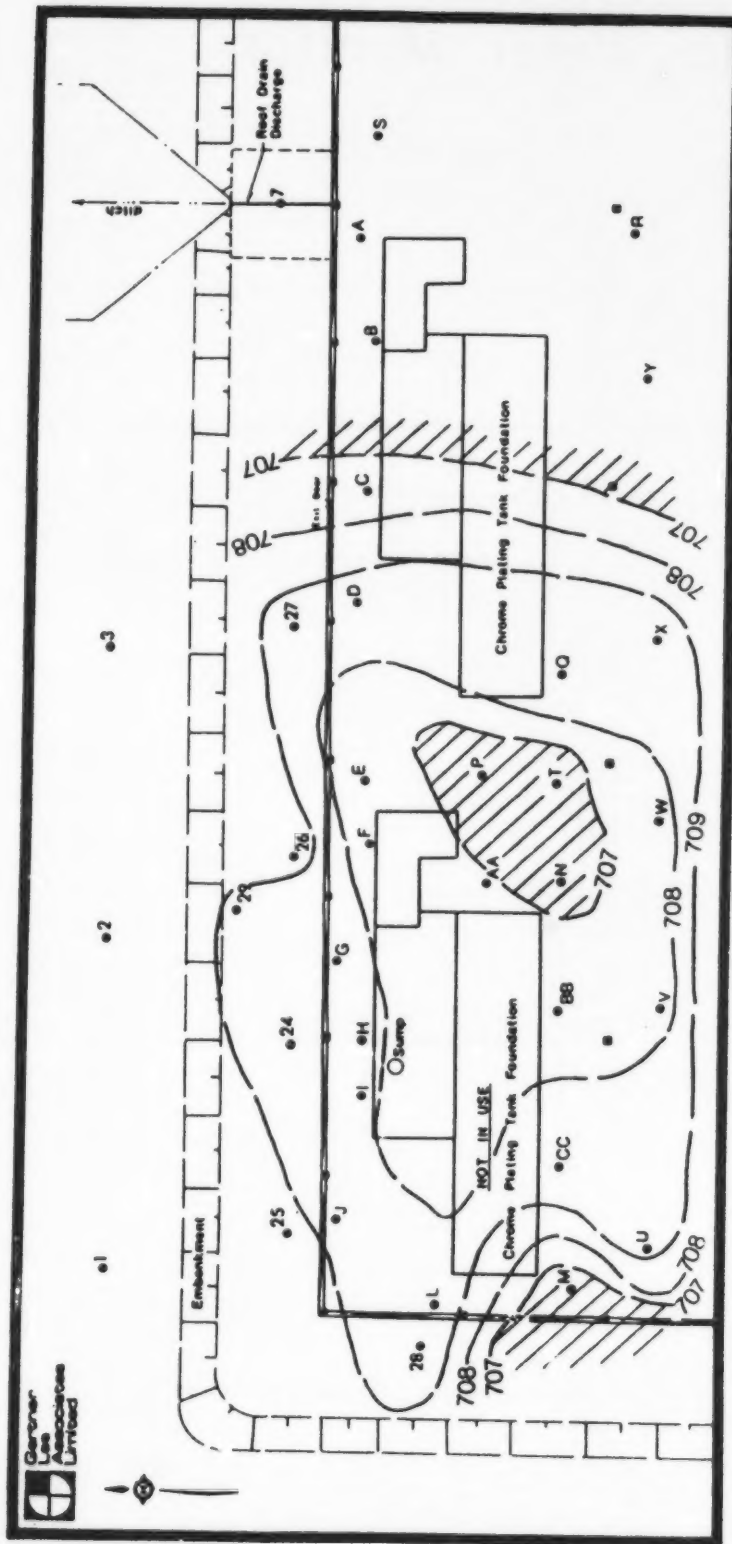


FIGURE 2

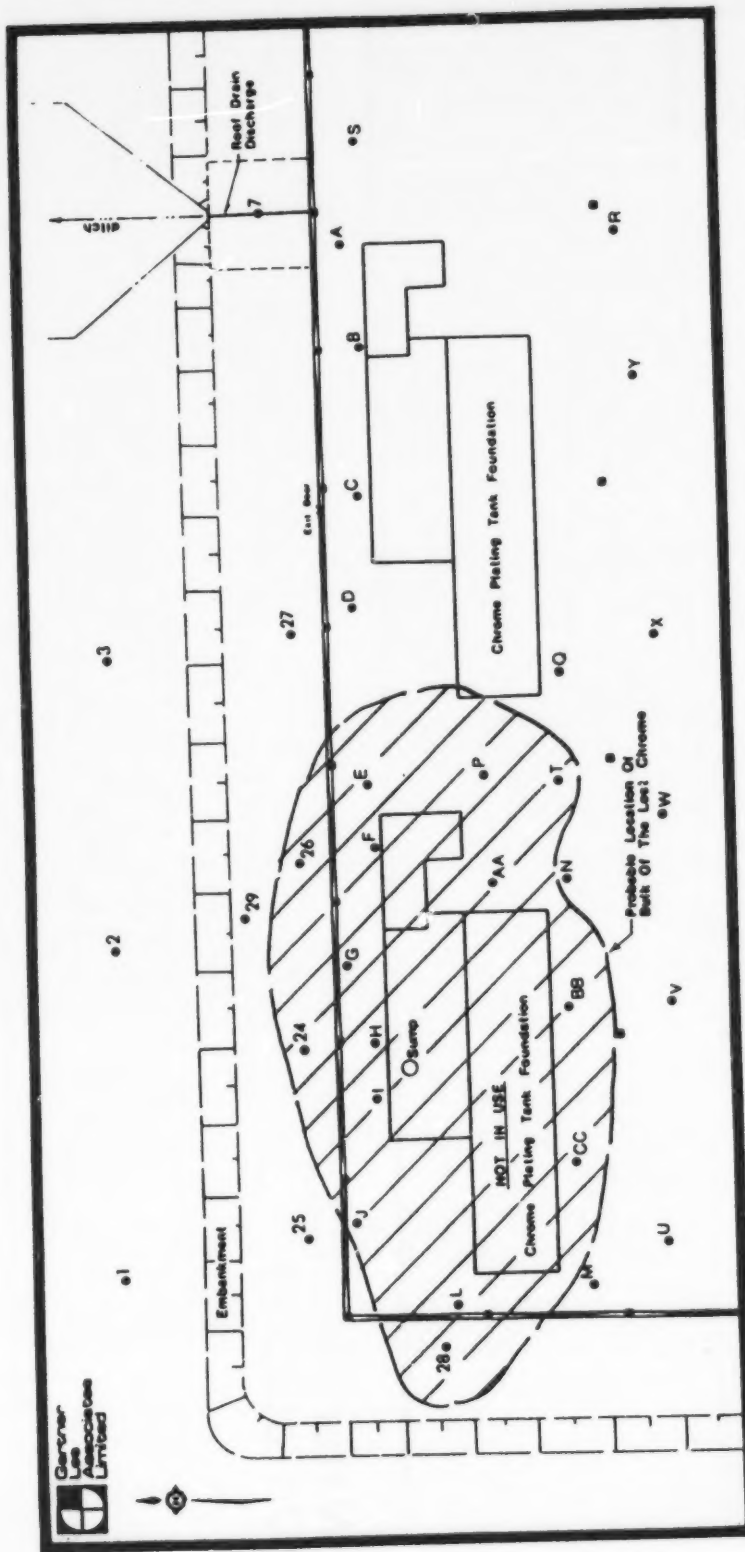
Gartner Lee Associates Limited



Water Table Contours
On Dec. 23, / 82

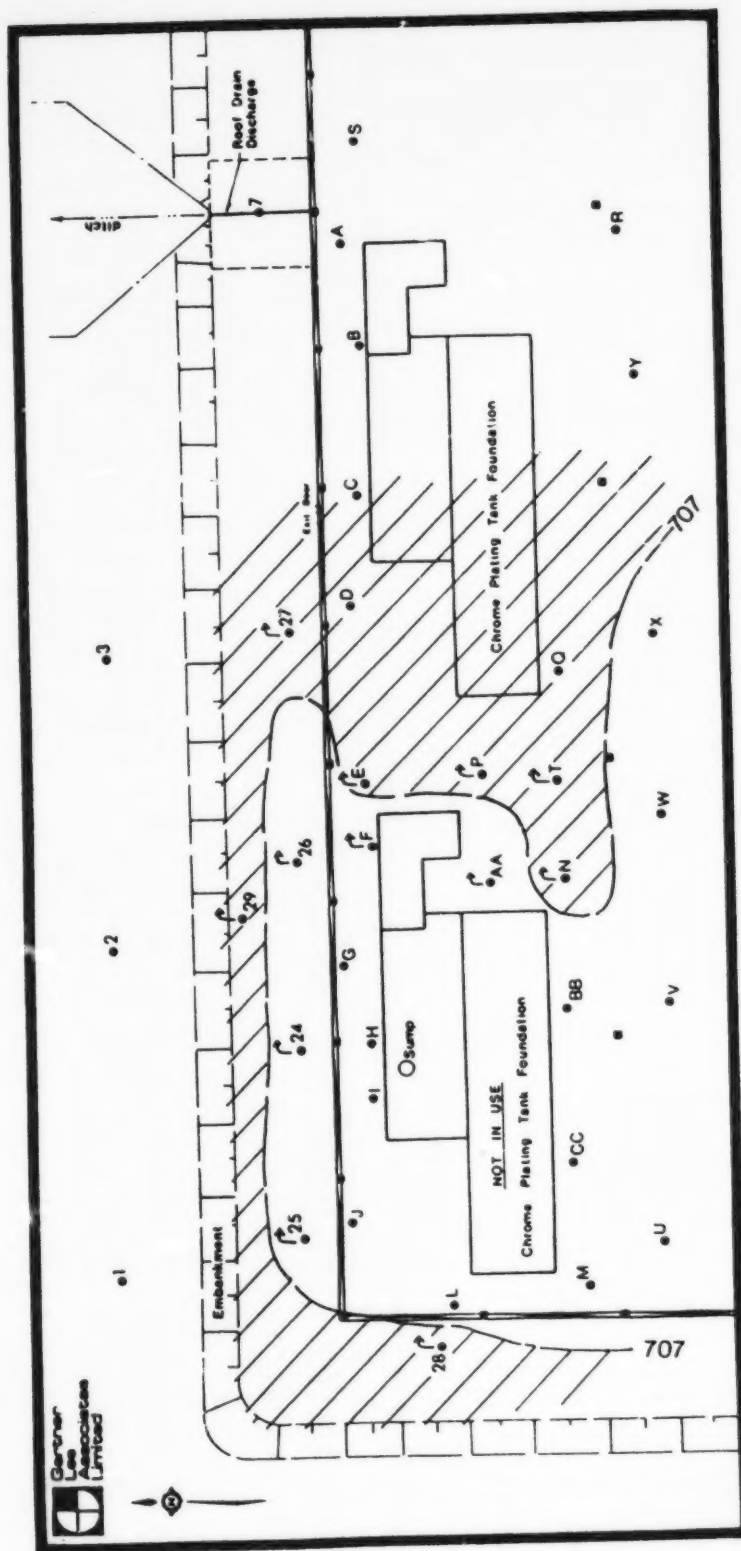
- Legend
- TEST HOLE
 - ANY AREAS IN EXAMINATION
 - FLOOD ELEVATION 713.0
 - SURFACE GRADE ELEVATION 708.0
 - BOTTOM OF GRAVITY LINE ELEVATION 707

FIGURE 3



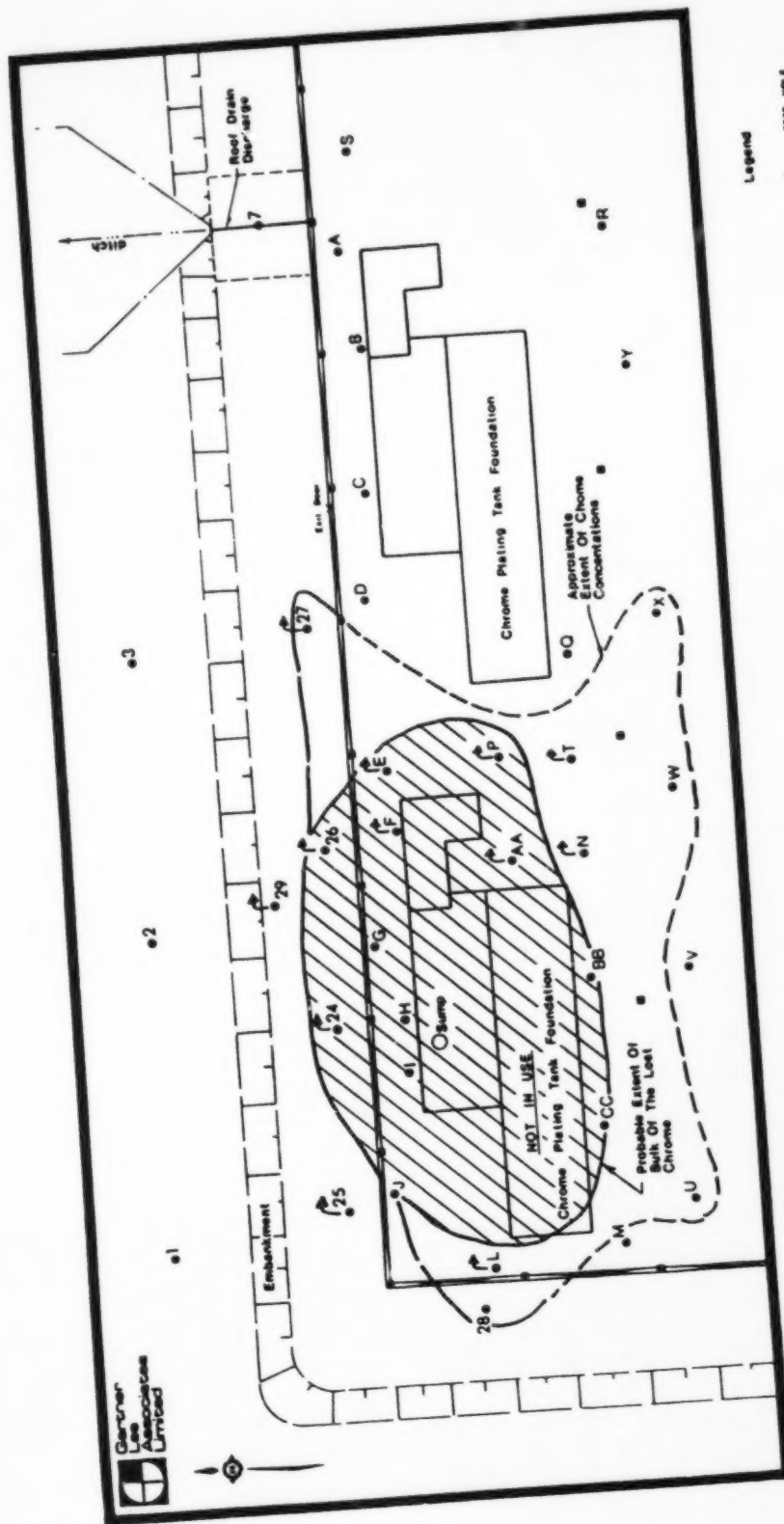
**Chrome Concentrations
On Dec. 23, /82**

FIGURE 4



Water Table Contours
On Jan. 19, /83

FIGURE 5



Chrome Concentrations
On Jan. 18, / 83

FIGURE 6

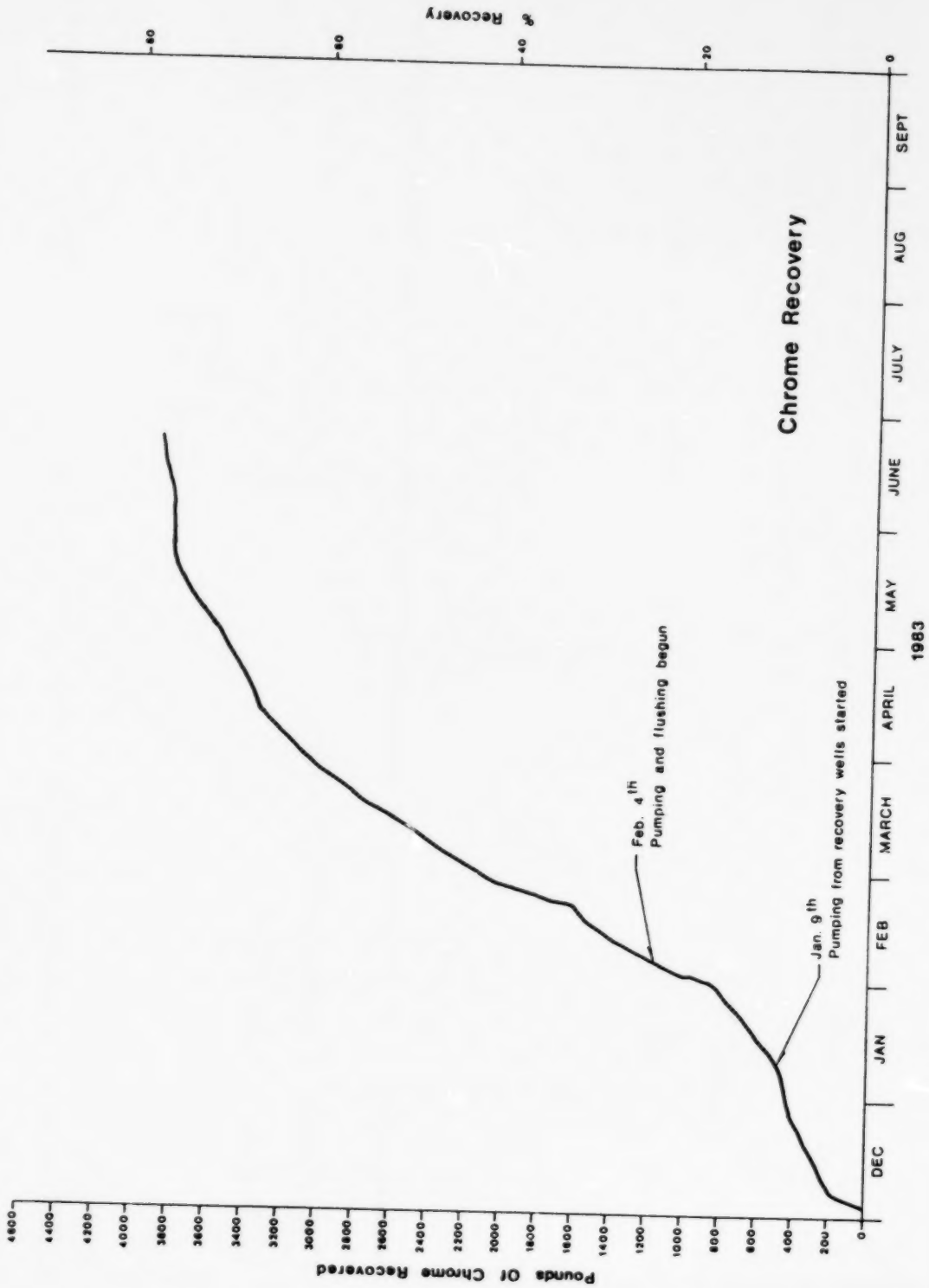
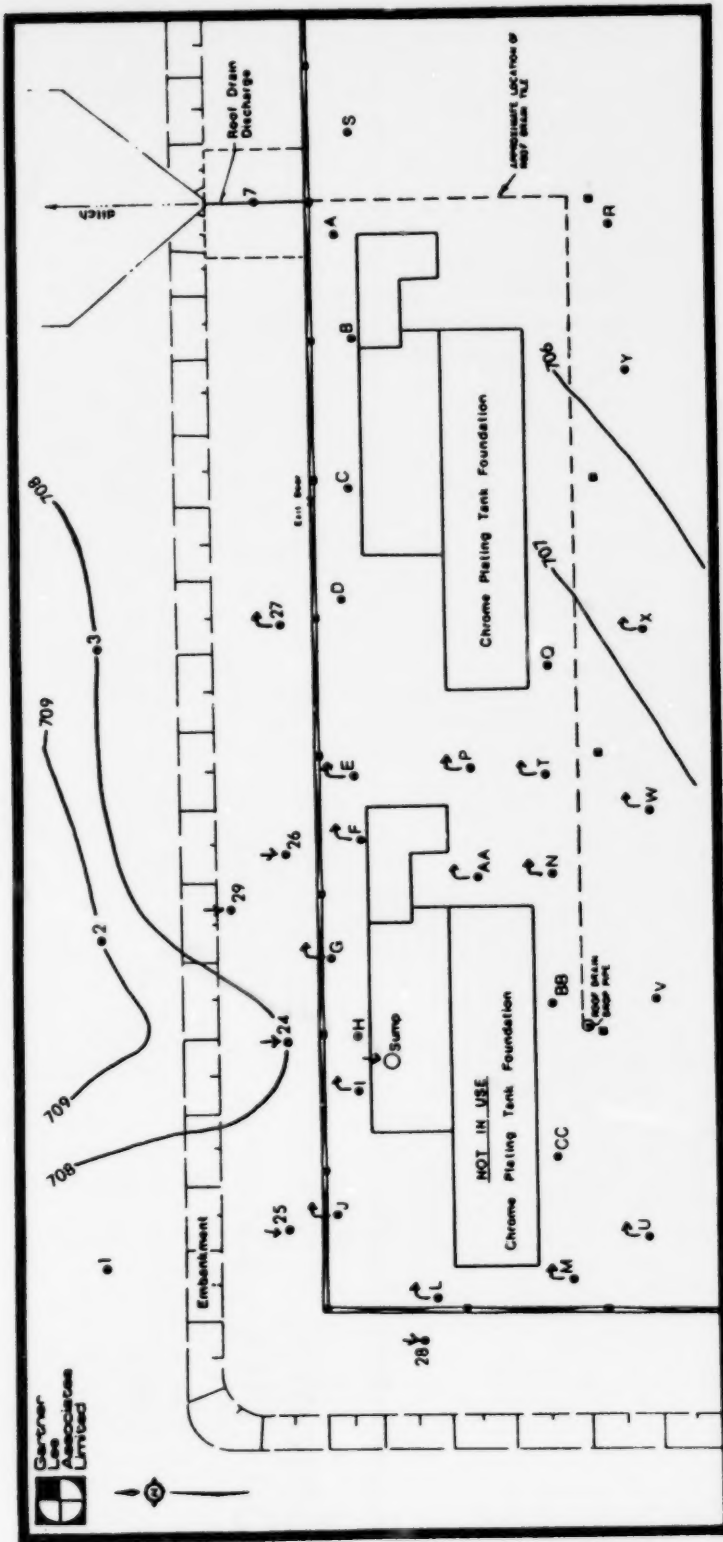
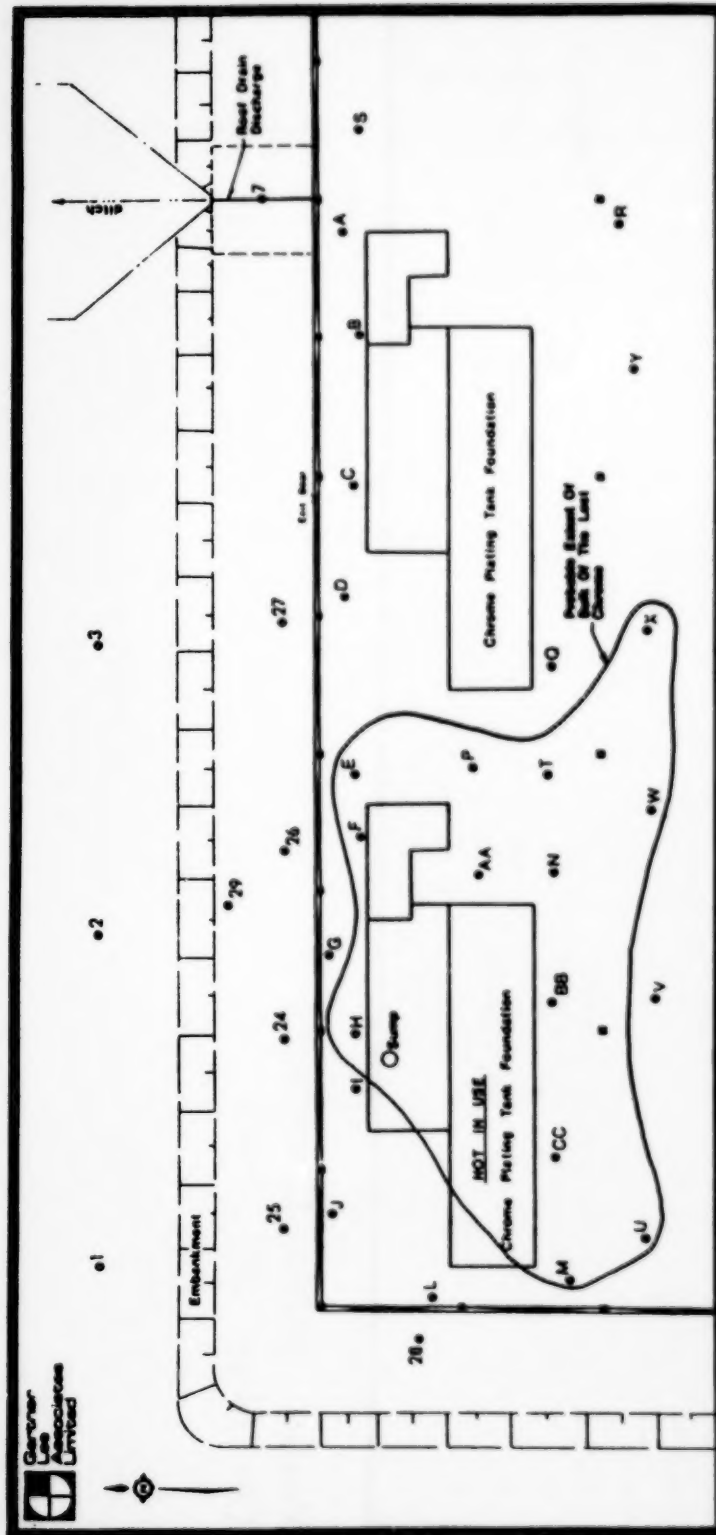


FIGURE 7



Water Table Contours
On May 27, / 83

FIGURE 8



**Chrome Concentrations
On May 13, / 83**

FIGURE 9

A SURVEY OF COUNTERMEASURES SYSTEMS FOR HAZARDOUS MATERIAL SPILLS

L.B. Solsberg
Hatfield Consultants Limited
West Vancouver, British Columbia

INTRODUCTION

The Survey of Countermeasures Systems for Hazardous Material Spills is a compendium of conceptual, prototype and commercially available response equipment. It was compiled in 1983-4 for the Environmental Protection Service by Mr. L.B. Solsberg and Mr. R.D. Parent who were then employed by S.L. Ross Environmental Research Limited. Mr. M.F. Fingas served as the EPS Scientific Authority for the project. The 1984 document, which is now being circulated for peer review, is based on a draft version originally prepared by M.M. Dillon Ltd. of Toronto and released for comment in February 1982. Funding to facilitate the final review and printing of the updated and revised Survey was provided by the American Association of Railways. It is expected that all data and comments will be incorporated into the 1984 edition by March 31, 1985 with publication of a final report soon after.

The Countermeasures Survey is primarily seen as a reference source or catalogue for persons with responsibilities relating to the purchase and/or application of spill cleanup technologies. To this end, the devices, materials and concepts included have been independently evaluated, have proven performance, or were judged to have potential merit by the authors and the Scientific Authority for hazardous material spill response.

Exclusions from the Survey generally covered:

- home remedies
- personal protection equipment
- detection, tracking and remote sensing hardware
- devices with exclusive oil spill use
- communications gear
- long-term prevention or disposal techniques

Time constraints associated with the project only allowed, in some cases, the review of equipment and materials representative of one particular group of countermeasures. Thus 15 general listings—actually comprehensive reviews—were prepared on subjects either too broad in scope to set down in detail or which would have required an arbitrary, and perhaps inappropriate, selection of few processes or hardware items. Similarly, time restrictions also resulted in North American companies and agencies being the primary contacts made.

The Survey is in no way intended as a comprehensive field manual for first responders nor is its application as such encouraged whatsoever. It should, however, assist in the selection/implementation of countermeasures as well as the assessment of future related research and development priorities.

All entries including the detailed, individual listings as well as the more general reviews, have been organized according to six main sections and 23 subsections. These reflect the cleanup operations to which they would likely be applied and in an order in which they might be considered for use:

- 1.0 CONTAINMENT
 - 1.1 Leak Mitigation
 - 1.2 Containment on Land
 - 1.3 Containment on Water
 - 1.4 Containment in Water
 - 1.5 Vapour Control
- 2.0 REMOVAL
 - 2.1 Removal from Land
 - 2.2 Skimming from Water
 - 2.3 Vacuum Systems
 - 2.4 Sorbents
 - 2.5 Dredging
 - 2.6 Removal from Water-Physical/Chemical Processes
 - 2.7 Removal from Water-Agents
 - 2.8 Fundamental Wastewater Treatment Techniques
- 3.0 TEMPORARY STORAGE
 - 3.1 Flexible Containers
 - 3.2 Rigid Wall Systems
 - 3.3 Liners
- 4.0 TRANSFER
 - 4.1 Transfer of Liquids
 - 4.2 Transfer of Gases
 - 4.3 Transfer Hoses
- 5.0 ULTIMATE DISPOSAL
 - 5.1 Incineration/Combustion
 - 5.2 Fixation: Solidification/Encapsulation
 - 5.3 Physical/Chemical Methods
 - 5.4 Biodegradation
- 6.0 ANCILLARY EQUIPMENT

In all, the 1984 Survey includes 162 separate entries as compared with 135 products in the 1982 draft report. At least 60 new listings now appear while 30 or more original entries have been eliminated for various reasons. The main differences between the first draft Survey and the most recent report can be summarized as follows according to each of the six main sections:

1.0 Containment

For spills on water, a general listing now describes spill containment barriers and their potential for application to chemical releases. Reference is also made to Environment Canada's Boom Catalogue rather than the old arbitrary listing of seven barriers almost all of which are inappropriate for most probable accident scenarios involving hazardous materials. Otherwise, this section incorporates only minor changes and several additions.

2.0 Removal

A totally revamped section on Removal considers eight categories of techniques designed to recover spilled chemical substances. It replaces the section on mechanical recovery that dealt with Recovery from Land, Recovery from Water-Floating Materials, and Recovery from Water-Sinking Materials. The numerous changes made include a more extensive section on land removal and general listings, which comprise "mini-studies", for mechanical skimmers,

small suction devices, large suction devices, sorbents (formerly a section under "Treatment"), dredging equipment and fundamental wastewater treatment techniques. These are organized along with other specific products according to the Section 2.0 headings described above. Again, most arbitrary selections have been excluded particularly in the case where only several devices have undergone limited testing. For example, the 15 oil skimmers previously included for recovering floating materials have been replaced by a broader scope approach which discusses the potential use of commercial units on chemical spills. It references the Environment Canada technical report "A Catalogue of Oil Skimmers". Section 2.0 now also includes physical/chemical processes and agents conceived for removing hazardous chemicals from water.

3.0 Temporary Storage

This section has been expanded to consist of three sub-sections which deal with flexible containers, rigid wall systems and liners rather than one more general section on storage. In addition to specific commercial items, general listings have been compiled for both flexible and rigid tanks as well as polymeric membranes.

4.0 Transfer

The original chapter on transfer was generally well done and essentially remains the same save for some new data included for old entries as well as a general listing on acid and chemical hoses.

5.0 Ultimate Disposal

The 1982 draft report presented a section entitled "Treatment" which was comprised of four subsections on "systems and processes", five subsections on "agents" and a concluding subsection on applicators. A mix was given of specific processes and agents such as incineration, sorbents and gelling agents along with categories of approaches such as removal from water and removal from soil. In the 1984 Survey, the old sections pertaining to removal have been moved, where appropriate, to the new Section 2.0, Removal. Included are sorbents which generally are not considered to be a treatment agent.

Section 5.0, Ultimate Disposal, was developed because it more closely ties in with the usual final stage of spill cleanup (exclusive of site restoration). The four new sections on incineration/combustion, fixation, physical/chemical methods and biodegradation describe techniques which cause the destruction of the released substance or otherwise render it innocuous. General listings comprehensively review fixation technology and composting and landfarming methods.

6.0 Ancillary Equipment

This new section concludes the Survey and replaces the former Section 5 entitled "Handling Devices". It has been expanded from two entries to ten entries and describes hardware that should facilitate spill response while not actually contacting or directly treating the spilled substance itself.

For each of the detailed, individual entries and several of the general listings, data have been provided appropriate to the following subsections:

- Applicability
- Description
- Operating Principle
- Physical Specifications
- Operating Specifications
- Status of Development and Usage
- Performance
- Availability and Commercial Information
- Other Data

For the most part, these are self-explanatory. In the case of "Applicability", this heading refers to the general behavioural group to which the device or concept should be considered for use, i.e. gases, soluble (Sol), floating (Fl) and sinking (Sk) liquids and solids. It was not found possible to correlate a list of 150 priority substances with each entry since information on compatibility or processing capability is usually lacking.

The "Description", for the most part, includes both narrative and graphic components. Special mention should be made of the contribution of Mr. B.A.K. Townshend of EPS who prepared 112 new technical drawings for the Survey. These are important to understanding the complexity of the technology, its relative size, and its principle of operation.

The individual entries are numbered to facilitate use of the catalogue as a guide as well as for easier cross-referencing. In this regard, two Indexes were compiled to further assist locating information. The first Index contains a detailed list of all entries arranged in numbered, sequential order according to cleanup operation. The second Index is organized on a company-by-company basis and should enable any entry to be referenced if the company name only is known.

The Survey also contains two brief Appendices providing additional information, one on cleanup contractors and a second listing Canadian chemical suppliers. Ten appendices previously included have been discarded since it was felt that either they did not provide data of direct relevance to the catalogue or could, in some cases, be incorporated as components of individual entries. The latter situation holds true for an appendix which dealt with the performance of foams as well as a separate summary table outlining the status of equipment development of all listings. Summary tables and appendices which described the suitability or compatibility of equipment and/or materials with priority substances have been excluded since arbitrary judgement was involved rather than a sound chemical engineering decision.

Recommendations

Recommendations arising from this work include the following:

- 1) The Countermeasures Survey should serve as a basic reference source on spill technology rather than as a field guide. If detailed data are sought, more indepth research is recommended using the contact information given in the catalogue.
- 2) This general area of cleanup technology is quickly evolving and efforts should be made to stay current with the many changes anticipated.
- 3) Because most of the specific devices, materials and concepts are relatively complex, future work should consider their study on an individual basis perhaps according to one specific approach within one cleanup phase (i.e. within containment, removal, disposal, etc.).
- 4) The Environmental Protection Service's current practice of investigating individual chemical substances should be continued including the examination of countermeasures systems for each substance. Selecting numerous hazardous materials as a basis for spill technology research is seen as being less productive.